

HYBRID ELECTROLYTE, METHOD FOR MANUFACTURING THE SAME, AND METHOD FOR MANUFACTURING ELECTROCHEMICAL ELEMENT USING THE SAME

Patent Number: ☐ [EP0921529](#), [A4](#)
 Publication date: 1999-06-09
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 Requested Patent: ☐ [WO9748106](#)
 Application Number: EP19970926249 19970613
 Priority Number(s): WO1997JP02056 19970613; JP19960152134 19960613; JP19970100397 19970417
 IPC Classification: H01B1/12
 EC Classification: [H01M10/40B](#), [H01M10/40](#)
 Equivalents: ☐ [US6299653](#)
 Cited Documents: [EP0730316](#); [US5429891](#)

Abstract

Disclosed is a hybrid electrolyte comprising a shaped porous polymer structure comprising a polymer matrix and a plurality of cells dispersed in the polymer matrix, the polymer matrix containing a crosslinked polymer segment and having a gel content in the range of from 20 to 75 %, wherein the shaped porous polymer structure is impregnated and swelled with an electrolytic liquid. A method for producing the hybrid electrolyte and a method for producing an electrochemical device comprising the hybrid electrolyte are also disclosed. The hybrid electrolyte of the present invention has a high ionic conductivity, an excellent stability under high temperature conditions and an excellent adherability to an electrode. Further, by the method of the present invention, the hybrid electrolyte having the above-mentioned excellent properties and an electrochemical device comprising such a hybrid electrolyte can be surely and effectively produced.

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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to a novel hybrid electrolyte. More particularly, the present invention is concerned with a novel hybrid electrolyte comprising a shaped porous polymer structure comprising a polymer matrix and a plurality of cells dispersed in the polymer matrix, the polymer matrix containing a crosslinked polymer segment and having a specific gel content, wherein the shaped porous polymer structure is impregnated and swelled with an electrolytic liquid. The present invention is also concerned with a method for producing the hybrid electrolyte and a method for producing an electrochemical device comprising the hybrid electrolyte.

[0002] The hybrid electrolyte of the present invention has a high ionic conductivity, an excellent stability under high temperature conditions and an excellent adherability to an electrode, so that the hybrid electrolyte of the present invention can be advantageously used as an electrolyte for various electrochemical devices, such as primary and secondary batteries (e.g., a lithium battery), a photoelectrochemical device and an electrochemical sensor. Further, by the method of the present invention, the hybrid electrolyte having the above-mentioned excellent properties and an electrochemical device comprising the same can be surely and effectively produced.

Prior Art

[0003] Recently, for reducing the size and weight of portable equipments, such as pocket telephones and personal computers, there has been a demand for a battery having high energy density. As a battery for meeting such a demand, lithium ion batteries have been developed. This type of battery has a structure in which a porous separator is disposed between the positive and negative electrodes, wherein the porous separator is not swelled with an electrolytic liquid. For preventing a leakage of the electrolytic liquid used for impregnating the separator, the commercially produced battery of this type has a battery structure wholly packaged in a very strong metallic casing having a large thickness.

[0004] On the other hand, so-called solid type batteries produced using a solid electrolyte functioning not only as an electrolyte but also as a separator are advantageously free from the danger of leakage of an electrolytic liquid. Therefore, it is expected that not only is a solid electrolyte useful for providing a battery having improved reliability and safety, but is also advantageous in that both the lamination of a solid electrolyte onto electrodes and the packaging of the resultant laminate to form a battery can be easily performed, wherein the thickness and weight of the battery can be reduced. Especially, a polymeric solid electrolyte comprising an ion-conductive polymer has excellent flexibility for processing and, therefore, not only can a laminate structure composed of the polymeric solid electrolyte and electrodes be easily produced, but also the polymeric solid electrolyte is capable of changing its morphology at an interface between the electrolyte and the electrodes in accordance with the volumetric change of the electrodes caused by the occlusion and release of ions by the electrodes, enabling the interface of the polymeric solid electrolyte to intimately fit over the electrodes without suffering delamination from the electrodes.

[0005] As such a polymeric solid electrolyte, an alkali metal salt complex of polyethylene oxide was proposed by Wright in British Polymer Journal, vol.7, p.319 (1975). Since then, researches on various skeletal materials for polymeric solid electrolytes have been energetically conducted. Examples of such skeletal materials include polyethers, such as polyethylene oxide and polypropylene oxide, polyphosphazene and polysiloxane. Generally, polymeric solid electrolytes are provided in the form of solid solutions of a solid electrolyte and a polymeric solid, wherein the solid electrolyte is considered to be uniformly dissolved in the polymeric solid, and are known as dry type polymeric electrolytes. However, these polymeric solid electrolytes have a problem in that the ionic conductivity of them is extremely low as compared to that of an electrolytic liquid. Therefore, a battery produced using such a polymeric solid electrolyte has problems in that it has a low charge/discharge

current density and has a high resistance.

[0006] For solving these problems, various attempts to improve the ionic conductivity of a polymeric solid electrolyte have been proposed, wherein the condition of the solid electrolyte is rendered similar to the condition of the electrolyte in the electrolytic liquid. For example, gelled solid electrolytes are known which are obtained by adding a solvent for the electrolyte (which solvent is capable of dissolving an electrolyte to form an electrolytic liquid) as a plasticizer to a polymer matrix so that the solvent and the polymer matrix together form a gel, wherein the solvent is used for increasing the dissociation of the electrolyte and promoting the molecular movement of the polymer, so that the ionic conductivity of the electrolyte can be increased (see, for example, Japanese Patent Application Laid-Open Specification No. 57-143356). As an example of such a gelled solid electrolyte, U.S. Patent No. 5,296,318 discloses a gelled solid electrolyte obtained by adding an electrolytic liquid to a vinylidene fluoride polymer so that the electrolytic liquid and the polymer together form a gel. Further, U.S. Patent No. 5,429,891 discloses a gelled solid electrolyte obtained by adding an electrolytic liquid to a crosslinked vinylidene fluoride polymer to thereby swell the crosslinked polymer so that the electrolytic liquid and the crosslinked polymer together form a gel. In general, when a battery comprising such a gelled solid electrolyte (i.e., a so-called hybrid electrolyte) is produced, a hybrid electrolyte comprising a crosslinked polymer swelled with an electrolytic liquid is produced, and then, a battery is assembled using the swelled hybrid electrolyte, electrodes, etc. With respect to the polymer matrix of such a hybrid electrolyte, a crosslinked polymer can be used. On the other hand, a method for producing a battery comprising a hybrid electrolyte layer is also known, wherein the hybrid electrolyte layer is formed by coating electrodes for the battery with a solution obtained by dissolving a non-crosslinked polymer, an electrolyte and a plasticizer in a low boiling point solvent, followed by removing the solvent by evaporation (see U.S. Patent No. 5,296,318). Each of these materials is electrochemically stable and has a high ionic conductivity, as compared to that of a conventional dry type solid electrolyte. However, the ionic conductivity of each of the above-mentioned hybrid electrolytes is still unsatisfactory, as compared to that of an electrolytic liquid. Further, a non-porous polymer matrix is used for each of the above-mentioned conventional hybrid electrolytes. Hence, the capacities of the batteries comprising such conventional hybrid electrolytes are disadvantageously low.

[0007] As a hybrid electrolyte having a high ionic conductivity, a material has been proposed, which comprises a gel phase (comprising a polymer and an electrolytic liquid) and a liquid phase (comprising an electrolytic liquid), wherein the liquid phase is dispersed in the gel phase. For example, Unexamined Japanese Patent Application Laid-Open Specification No. 8-250127 describes the use of a vinylidene fluoride porous polymer sheet as a polymer matrix of a solid electrolyte. In this document, a description is made with respect to a method for impregnating a porous polymer sheet with an electrolytic liquid under high temperature conditions, to thereby form a hybrid electrolyte (comprising the porous polymer sheet impregnated and swelled with the electrolytic liquid), which is similar to the hybrid electrolyte of the present invention. Further, Unexamined Japanese Patent Application Laid-Open Specification No. 6-150939 discloses a method for producing a hybrid (solid) electrolyte, in which a porous structure comprising a crosslinked polymer containing polar units is used as a matrix for the hybrid (solid) electrolyte. However, in the method described in these documents, in order to retain an electrolytic liquid in the matrix, a crosslinked porous polymer sheet as the matrix is immersed in an excess amount of an electrolytic liquid under conditions at which a non-crosslinked polymer segment contained in the crosslinked porous polymer sheet can be dissolved in the electrolytic liquid. In the hybrid electrolyte thus obtained, the non-crosslinked polymer segment contained in the crosslinked porous polymer sheet (which segment is capable of imparting the resultant electrolyte with an adherability to electrodes) is dissolved into the electrolytic liquid during the immersion, so that the adherence strength of the resultant electrolyte to electrodes disadvantageously becomes low.

[0008] Further, Unexamined Japanese Patent Application Laid-Open Specification No. 8-195220 discloses a method for producing a hybrid electrolyte comprising a porous polymer matrix, which comprises dispersing a non-crosslinked polyacrylonitrile in an electrolytic liquid to thereby obtain a dispersion; coating a stainless steel substrate with the obtained dispersion and heating the dispersion coated on the stainless steel substrate to dissolve the non-crosslinked polyacrylonitrile (which is contained in the dispersion coated on the stainless steel substrate) into the electrolytic liquid, to thereby form a homogeneous solution; cooling the thus formed solution on the stainless steel substrate to thereby form a hybrid electrolyte layer comprising a polymer matrix comprising the non-crosslinked polyacrylonitrile and the electrolytic liquid retained in the polymer matrix; and pricking holes in the hybrid electrolyte layer (by means of a thin stainless needle) in a condition where the hybrid electrolyte layer is immersed in a solution of an electrolyte, so that the polymer matrix of the hybrid electrolyte layer is rendered porous, to thereby obtain a hybrid electrolyte comprising the porous polymer matrix and the electrolytic liquid contained therein. However, in this method, it is required to dissolve a polyacrylonitrile into an electrolytic liquid and, therefore, it is required to use a non-crosslinked polyacrylonitrile. Further, in this method, it is difficult to introduce a crosslinked structure into the polyacrylonitrile constituting the polymer matrix of the hybrid electrolyte obtained by this method. Therefore,

the non-crosslinked polyacrylonitrile constituting the porous polymer matrix of the hybrid electrolyte is likely to be dissolved into the electrolytic liquid or fused under high temperature conditions, so that there is disadvantageously a danger that the hybrid electrolyte obtained by this method suffers distortion, thereby causing shutting or short-circuiting of the pores of the hybrid electrolyte.

[0009] Further, each of the above-mentioned various types of hybrid electrolytes is constructed with a polymer which is already swelled with an electrolytic liquid, so that the mechanical strength of the electrolyte is disadvantageously low and, hence, it is not easy to handle the hybrid electrolyte for laminating the hybrid electrolyte onto electrodes in the assembling of a battery. In particular, it is extremely difficult to produce the above-mentioned hybrid electrolyte in the form of a thin sheet so as to increase the energy density of the hybrid electrolyte. With respect to the method comprising coating an electrolyte with a solution of a polymer and an electrolyte in a solvent, the handling of the electrolyte is easy. However, from the viewpoint of safety, this method is not preferred because a low boiling point solvent which is combustible, such as THF, is used.

[0010] On the other hand, an attempt to prevent the electrolytic liquid in a solid electrolyte from leakage has been proposed, wherein a liquid ion conductor is filled in the pores of a porous polymer sheet of the solid electrolyte so that it can be retained in the porous polymer sheet by the capillary action. For example, a microporous polymer sheet made of a material having a high mechanical strength, such as a polyolefin, and having a through-hole diameter of 0.1 mm or less is provided, and the pores of the microporous polymer sheet are filled up with an ion transferring medium to thereby form a thin electrolyte sheet (Unexamined Japanese Patent Application Laid-Open Specification No. 1-158051). With respect to the solid electrolyte of this type, the mechanical strength is large; however, a large number of pores in the microporous polymer sheet form complicated labyrinthian passages and, therefore, ions have to pass through the electrolytic liquid phase in such complicated labyrinthian passages, so that the above-mentioned solid electrolyte has a defect in that the ionic conductivity thereof is disadvantageously low.

SUMMARY OF THE INVENTION

[0011] In this situation, the present inventors have made extensive and intensive studies toward developing a hybrid electrolyte which is free from difficult problems accompanying the above-mentioned prior art techniques and has not only a high ionic conductivity, but also an excellent stability under high temperature conditions and an excellent adherability to an electrode, and a method for surely and effectively producing the hybrid electrolyte and an electrochemical device, such as a battery, comprising the hybrid electrolyte. As a result, it has unexpectedly been found that a hybrid electrolyte, which comprises a shaped porous polymer structure comprising a polymer matrix and a plurality of cells dispersed in the polymer matrix, wherein the polymer matrix contains a crosslinked polymer segment and has a gel content in the range of from 20 to 75 %, and wherein the polymer matrix is impregnated and swelled with an electrolytic liquid selected from the group consisting of a solution of an electrolyte in water or a non-aqueous solvent and a liquid electrolyte, exhibits a high ionic conductivity, an excellent stability under high temperature conditions and an excellent adherability to an electrode.

[0012] Further, it has also been found that the above-mentioned hybrid electrolyte can be surely and effectively produced by a method which comprises impregnating the above-mentioned shaped porous polymer structure with the above-mentioned electrolytic liquid under predetermined non-swelling temperature and pressure conditions at which the shaped porous polymer structure is substantially insusceptible to swelling with the electrolytic liquid, thereby obtaining an impregnated, shaped porous polymer structure; and holding the impregnated, shaped porous polymer structure under predetermined swelling temperature and pressure conditions at which the shaped porous polymer structure is susceptible to swelling with the electrolytic liquid.

[0013] Still further, it has unexpectedly been found that an electrochemical device comprising the above-mentioned hybrid electrolyte can be surely and effectively produced by a method which comprises impregnating the above-mentioned shaped porous polymer structure with the above-mentioned electrolytic liquid under predetermined non-swelling temperature and pressure conditions at which the shaped porous polymer structure is substantially insusceptible to swelling with the electrolytic liquid, thereby obtaining an impregnated, shaped porous polymer structure; laminating the impregnated, shaped porous polymer structure to an electrode to thereby obtain a laminate structure; and holding the laminate structure under predetermined swelling temperature and pressure conditions at which the shaped porous polymer structure is susceptible to swelling with the electrolytic liquid.

[0014] Furthermore, it has unexpectedly been found that an electrochemical device comprising the above-mentioned hybrid electrolyte can be surely and effectively produced by a method which comprises laminating the above-mentioned shaped porous polymer structure to an electrode to thereby obtain a laminate structure; impregnating the laminate structure with the above-mentioned electrolytic liquid under predetermined non-swelling temperature and pressure conditions at which the shaped porous polymer structure is substantially insusceptible to swelling with the electrolytic liquid; and holding the impregnated laminate structure under predetermined swelling temperature and pressure conditions at which the shaped porous polymer structure is susceptible to swelling with the electrolytic liquid.

[0015] The present invention is completed based on the above-mentioned findings.

[0016] Therefore, it is an object of the present invention to provide a hybrid electrolyte which exhibits a high ionic conductivity, an excellent stability under high temperature conditions and an excellent adherability to an electrode.

[0017] It is another object of the present invention to provide a method for surely and effectively producing a hybrid electrolyte having the above-mentioned properties.

[0018] It is still another object of the present invention to provide a method for surely and effectively producing an electrochemical device, such as a battery, comprising a hybrid electrolyte having the above-mentioned properties.

[0019] The foregoing and other objects, feature and advantages of the present invention will be apparent to those skilled in the art from the following detailed description and appended claims.

DETAILED DESCRIPTION OF THE INVENTION

[0020] In an essential aspect of the present invention, there is provided a hybrid electrolyte which comprises a shaped porous polymer structure comprising a polymer matrix and a plurality of cells dispersed in the polymer matrix, the polymer matrix containing a crosslinked polymer segment and having a gel content in the range of from 20 to 75 %; and an electrolytic liquid selected from the group consisting of a solution of an electrolyte in water or a non-aqueous solvent and a liquid electrolyte, wherein the shaped porous polymer structure is impregnated and swelled with the electrolytic liquid.

[0021] For easy understanding of the present invention, the essential features and various embodiments of the present invention are enumerated below.

1. A hybrid electrolyte comprising:

a shaped porous polymer structure comprising a polymer matrix and a plurality of cells dispersed in the polymer matrix, the polymer matrix containing a crosslinked polymer segment and having a gel content in the range of from 20 to 75 %, and
an electrolytic liquid selected from the group consisting of a solution of an electrolyte in water or a non-aqueous solvent and a liquid electrolyte,
wherein the shaped porous polymer structure is impregnated and swelled with the electrolytic liquid.

2. The hybrid electrolyte according to item 1 above, wherein the polymer matrix has a gel content in the range of from 30 to 70 % by weight.

3. The hybrid electrolyte according to item 1 above, wherein the polymer matrix has a gel content in the range of from 35 to 65 % by weight.

4. The hybrid electrolyte according to any one of items 1 to 3 above, wherein the cells of the polymer matrix comprise open cells which form through-holes passing through the shaped porous polymer structure.

5. The hybrid electrolyte according to any one of items 1 to 4 above, wherein the shaped porous polymer structure has a void ratio of from 30 to 95 %.

6. The hybrid electrolyte according to any one of items 1 to 5 above, which is in the form of a sheet having a thickness of from 1 to 500 μ m.

7. The hybrid electrolyte according to any one of items 1 to 6 above, wherein the polymer matrix comprises a vinylidene fluoride polymer or an acrylonitrile polymer.

8. The hybrid electrolyte according to any one of items 1 to 7 above, wherein the crosslinked polymer segment has a crosslinked structure formed by electron beam irradiation or gamma-ray irradiation.

9. A method for producing a hybrid electrolyte, which comprises:

impregnating a shaped porous polymer structure, which comprises a polymer matrix and a plurality of cells dispersed in the polymer matrix, wherein the polymer matrix contains a crosslinked polymer segment, with an electrolytic liquid selected from the group consisting of a solution of an electrolyte in water or a non-aqueous solvent and a liquid electrolyte under predetermined non-swelling temperature and pressure conditions at which the shaped porous polymer structure is substantially insusceptible to swelling with the electrolytic liquid, thereby obtaining an impregnated, shaped porous polymer structure; and holding the impregnated, shaped porous polymer structure under predetermined swelling temperature and pressure conditions at which the shaped porous polymer structure is susceptible to swelling with the electrolytic liquid.

10. The method according to item 9 above, wherein the cells of the polymer matrix comprise open cells which form through-holes passing through the shaped porous polymer structure.

11. The method according to item 9 or 10 above, wherein the polymer matrix comprises a vinylidene fluoride polymer or an acrylonitrile polymer.

12. The method according to any one of items 9 to 11 above, wherein the electrolytic liquid is selected from the group consisting of a solution of an electrolyte in a non-aqueous solvent and a liquid electrolyte.

13. A method for producing a hybrid electrolyte, which comprises:

impregnating a shaped porous polymer structure, which comprises a polymer matrix and a plurality of cells dispersed in the polymer matrix, wherein the polymer matrix comprises a vinylidene fluoride polymer or an acrylonitrile polymer and contains a crosslinked polymer segment, with an electrolytic liquid selected from the group consisting of a solution of an electrolyte in a non-aqueous solvent and a liquid electrolyte at a temperature of 35 DEG C or less under atmospheric pressure, thereby obtaining an impregnated, shaped porous polymer structure; and heating the impregnated, shaped porous polymer structure at a temperature of 80 DEG C or more under atmospheric pressure.

14. The method according to item 13 above, wherein the cells of the polymer matrix comprise open cells which form through-holes passing through the shaped porous polymer structure.

15. The method according to item 13 or 14 above, wherein the impregnated, shaped polymer structure is heated at a temperature of 90 DEG C or more.

16. A hybrid electrolyte which is substantially the same as that produced by the method of any one of claims 9 to 15.

17. A method for producing an electrochemical device, which comprises:

impregnating a shaped porous polymer structure, which comprises a polymer matrix and a plurality of cells dispersed in the polymer matrix, wherein the polymer matrix contains a crosslinked polymer segment, with an electrolytic liquid selected from the group consisting of a solution of an electrolyte in water or a non-aqueous solvent and a liquid electrolyte under predetermined non-swelling temperature and pressure conditions at which the shaped porous polymer structure is substantially insusceptible to swelling with the electrolytic liquid, thereby obtaining an impregnated, shaped porous polymer structure; laminating the impregnated, shaped porous polymer structure to an electrode to thereby obtain a laminate structure; and holding the laminate structure under predetermined swelling temperature and pressure conditions at which the shaped porous polymer structure is susceptible to swelling with the electrolytic liquid.

18. The method according to item 17 above, wherein the polymer matrix comprises a vinylidene fluoride polymer or an acrylonitrile polymer.

19. A method for producing an electrochemical device, which comprises:

impregnating a shaped porous polymer structure, which comprises a polymer matrix and a plurality of cells dispersed in the polymer matrix, wherein the polymer matrix comprises a vinylidene fluoride polymer or an acrylonitrile polymer and contains a crosslinked segments, with an electrolytic liquid selected from the group consisting of a solution of an electrolyte in a non-aqueous liquid and a liquid electrolyte at a temperature of 35 DEG C or less under atmospheric pressure, thereby obtaining an impregnated, shaped porous polymer structure; laminating the impregnated, shaped porous polymer structure to an electrode to thereby obtain a laminate structure; and heating the laminate structure at a temperature of 80 DEG C or more under atmospheric pressure.

20. The method according to item 19 above, wherein the laminate structure is heated at 90 DEG C or more.

21. A method for producing an electrochemical device, which comprises:

laminating a shaped porous polymer structure, which comprises a polymer matrix and a plurality of cells dispersed in the polymer matrix, wherein the polymer matrix contains a crosslinked polymer segment, to an electrode to thereby obtain a laminate structure;
impregnating the laminate structure with an electrolytic liquid selected from the group consisting of a solution of an electrolyte in water or a non-aqueous solvent and a liquid electrolyte under predetermined non-swelling temperature and pressure conditions at which the shaped porous polymer structure is substantially insusceptible to swelling with the electrolytic liquid, thereby obtaining an impregnated laminate structure; and
holding the impregnated laminate structure under predetermined swelling temperature and pressure conditions at which the shaped porous polymer structure is susceptible to swelling with the electrolytic liquid.

22. The method according to item 21 above, wherein the polymer matrix comprises a vinylidene fluoride polymer or an acrylonitrile polymer.

23. A method for producing an electrochemical device, which comprises:

laminating a shaped porous polymer structure, which comprises a polymer matrix and a plurality of cells dispersed in the polymer matrix, wherein the polymer matrix comprises a vinylidene fluoride polymer or an acrylonitrile polymer and contains a crosslinked polymer segment, to an electrode to thereby obtain a laminate structure;
impregnating the laminate structure with an electrolytic liquid selected from the group consisting of a solution of an electrolyte in a non-aqueous solvent and a liquid electrolyte at a temperature of 35 DEG C or less under atmospheric pressure, thereby obtaining an impregnated laminate structure; and
heating the impregnated laminate structure at a temperature of 80 DEG C or more under atmospheric pressure.

24. The method according to item 23 above, wherein the impregnated laminate structure is heated at a temperature of 90 DEG C or more.

25. The method according to any one of items 17 to 24 above, wherein the electrochemical device is a battery comprising a positive electrode and a negative electrode.

26. The method according to item 25 above, wherein the battery is a non-aqueous battery.

27. The method according to item 26 above, wherein the battery is a lithium ion secondary battery.

28. The method according to any one of items 17 to 27 above, wherein the electrochemical device has an electrode having a current collector and wherein the current collector is a mesh current collector.

29. An electrochemical device, which is substantially the same as that produced by the method of any one of claims 17 to 27.

[0022] The hybrid electrolyte of the present invention has intermediate properties as between a dry type solid electrolyte (containing no liquid) and a conventional liquid electrolyte (i.e., an electrolytic liquid selected from the group consisting of a solution of an electrolyte in water or a non-aqueous solvent). That is, the hybrid electrolyte of the present invention is a polymeric solid electrolyte containing a solvent, preferably a high boiling point solvent, in a large amount, wherein it is free from a danger that the polymer moiety of the electrolyte does not flow out from the electrolyte as a solution of the polymer in the solvent. The hybrid electrolyte of the present invention assumes a gel form despite containing an electrolytic liquid in a large amount, so that the retention of the electrolytic liquid in the solid electrolyte is increased. More specifically, the hybrid electrolyte of the present invention is a hybrid electrolyte which comprises a shaped porous polymer structure comprising a polymer matrix and a plurality of cells dispersed in the polymer matrix, the polymer matrix containing a crosslinked polymer segment and having a gel content in the range of from 20 to 75 %; and an electrolytic liquid selected from the group consisting of a solution of an electrolyte in water or a non-aqueous solvent and a liquid electrolyte, wherein the shaped porous polymer structure is impregnated and swelled with the electrolytic liquid.

[0023] Hereinbelow, a description is made with respect to the term "swelling" in the present invention. In general, when a crosslinked polymer is swelled with an excess amount of a solvent or solution, the volume of the polymer is drastically increased. In many cases, the resultant swelled, crosslinked polymer is expanded in all directions. However, when the crosslinked polymer has sustained a stress due, for example, to a stretching, the stress is relieved by the swelling and, in some specific directions, it is sometimes possible for the crosslinked polymer to shrink by the swelling. In any case, when a crosslinked polymer is swelled with an excess amount of a solvent or solution, the crosslinked polymer is likely to suffer large dimensional change. In the present invention, after immersing the shaped porous polymer structure in an electrolytic liquid under

predetermined temperature and pressure conditions (wherein the volume of the electrolytic liquid is 100 times or more as large as the volume of the outer profile of the shaped porous polymer structure), the change (%) in the longitudinal length of the shaped porous polymer structure, relative to the longitudinal length measured before the immersion, is determined. If the change exceeds 10 %, the shaped porous polymer structure is defined as being susceptible to swelling with the electrolytic liquid under the above-mentioned predetermined conditions.

[0024] On the other hand, whether or not the shaped porous polymer structure of a produced hybrid electrolyte has been impregnated and swelled with an electrolytic liquid, can be determined by a method in which the impregnated electrolytic liquid is removed from the produced hybrid electrolyte by extraction, followed by drying at room temperature to obtain the shaped porous polymer structure, and the degree of shrinkage of the obtained shaped porous polymer structure is determined. Specifically, in the present invention, the degree of shrinkage of a shaped porous polymer structure is obtained as follows. A produced hybrid electrolyte is immersed in a solvent, which is capable of extracting the electrolytic liquid but not capable of dissolving the polymer matrix, for 30 minutes or more to thereby extraction-remove the impregnated electrolytic liquid from the hybrid electrolyte, followed by drying in vacuum to thereby obtain a dried polymer matrix. The change in the longitudinal length of the above-obtained dried polymer matrix (shaped porous polymer structure), relative to the longitudinal length of the electrolytic liquid-impregnated hybrid electrolyte, is determined. This change (%) is defined as the degree of shrinkage of the shaped porous polymer structure. In the present invention, the hybrid electrolyte, which exhibits the above-defined degree of shrinkage of the shaped porous polymer structure of more than 10 %, is defined as being impregnated and swelled with an electrolytic liquid.

[0025] In general, a hybrid electrolyte, which is used as an electrolyte for the so-called polymer battery (i.e., a battery comprising a solid electrolyte containing a polymer), is in the form of a sheet or the like. In this case, it is difficult to mechanically keep the hybrid electrolyte in contact with electrodes and, therefore, the hybrid electrolyte is required to be adhered to electrodes. The hybrid electrolyte is generally adhered to electrodes by heating the hybrid electrolyte to a temperature in the range of from approximately 50 to 200 DEG C (or, some specific types of hybrid electrolytes are adhered to electrodes at room temperature) under a pressure in the range of from 0.1 to 20 kg/cm. In connection with this adhesion, when the hybrid electrolyte is adhered to electrodes by heating, a portion of the polymer used in the hybrid electrolyte may be melted so as to function as an adhesive. The adherability of the hybrid electrolyte to the electrode varies, as described below, depending on the gel content of a polymer matrix of the shaped porous polymer structure in the hybrid electrolyte, wherein the polymer matrix contains a crosslinked polymer segment.

[0026] The polymer matrix in the hybrid electrolyte of the present invention is required to have a gel content in the range of from 20 to 75 %, wherein the upper limit of the gel content is preferably 70 %, more preferably 65 %, and the lower limit of the gel content is preferably 30 %, more preferably 35 %. When the gel content of the hybrid electrolyte is more than 75 %, it is difficult to adhere the hybrid electrolyte to electrodes by heating, so that the adherence strength of the hybrid electrolyte with the electrodes is disadvantageously lowered. On the other hand, when the gel content of the hybrid electrolyte is less than 20 %, the thermal stability of the hybrid electrolyte becomes low, so that the hybrid electrolyte is likely to suffer distortion during the heating.

[0027] As described above, the hybrid electrolyte of the present invention comprises a shaped porous polymer structure comprising a polymer matrix and a plurality of cells dispersed in the polymer matrix, the polymer matrix being impregnated and swelled with an electrolytic liquid. The electrolytic liquid is present not only in the polymer matrix of the shaped porous polymer structure but also in the plurality of cells. The polymer matrix of the shaped porous polymer structure contains a crosslinked polymer segment which is introduced into the polymer by an appropriate crosslinking treatment. There is no limitation with respect to the type of the above-mentioned polymer to be subjected to the crosslinking treatment, as long as, after the crosslinking treatment, the polymer can be swelled with an electrolytic liquid. It is preferred that the polymer is electrochemically stable and exhibits a high ion-conductivity. Examples of such polymers include a poly(ethylene oxide), a polypropylene oxide, a vinylidene fluoride polymer, an acrylonitrile polymer, an oligo(ethylene oxide) poly(meth)acrylate, a poly(ethylene imine), a poly alkylene sulfide, a polyphosphazene and a polysiloxane each having an oligo(ethylene oxide) side chain, polymers each having ionic groups in the molecule, such as Nafion (manufactured and sold by Du Pont, U.S.A.), Flemion (manufactured and sold by Asahi Glass Co., Ltd., Japan) and the like. A vinylidene fluoride polymer and an acrylonitrile polymer include not only a homopolymer but also a copolymer. For example, a vinylidene fluoride-hexafluoropropylene copolymer, a vinylidene fluoride-trifluoroethylene copolymer, an acrylonitrile-(meth)acrylate copolymer, an acrylonitrile-styrene copolymer and the like can also be used. When a polymer having ionic groups in the molecule is used for producing a lithium ion battery, each of the ionic groups is preferably in the form of a lithium salt. Among these polymers, a vinylidene fluoride polymer, such as a poly(vinylidene fluoride), a

vinylidene fluoride-hexafluoropropylene copolymer or the like, and an acrylonitrile polymer, such as polyacrylonitrile, an acrylonitrile(meth)acrylate copolymer, an acrylonitrile-styrene copolymer or the like are preferred, due to the high ionic conductivity and excellent mechanical strength thereof. A vinylidene fluoride polymer is more preferred.

[0028] The polymer is subjected to a crosslinking treatment and converted to a polymer containing a crosslinked polymer segment. Introduction of the crosslinked structure into the polymer enhances the stability of a hybrid electrolyte under high temperature conditions. If the polymer is not crosslinked, when a battery comprising the hybrid electrolyte experiences high temperature conditions, the performance of the battery is likely to irreversibly change, or occasionally, a short-circuiting of the battery occurs due to the melting of the polymer. The introduction of the crosslinked structure can be conducted at any stage, for example, during polymerization, or before or after the shaping of a polymer for producing the shaped porous polymer structure. The crosslinked structure can be introduced into a shaped porous polymer structure which is swelled with an electrolytic liquid, a plasticizer and the like. Examples of methods for crosslinking treatment include a method in which a crosslinked structure is formed by conducting the polymerization of the monomer (and comonomer) in the presence of an additional multifunctional monomer; a method in which a crosslinked structure is formed by the irradiation of a radiation energy, such as electron beams, gamma-rays, X-rays, ultraviolet rays or the like after polymerization; and a method in which a crosslinked structure is formed by introducing a radical initiator into a polymer after the polymerization for producing the polymer, and heating or irradiating (with radiation energy) the polymer containing the radical initiator, to thereby effect a reaction for crosslinking. When the introduction of the crosslinked structure into the polymer is conducted after the polymerization for producing the polymer, it can be conducted in the presence of monofunctional and/or multifunctional monomer(s) which is/are newly added. Among these methods for crosslinking treatment, from a viewpoint of decreasing the amount of any remaining impurities or unreacted functional groups, a method in which a crosslinked structure is formed by the irradiation of a radiation energy, such as electron beams, gamma-rays, X-rays, ultraviolet rays or the like after polymerization is preferred. Further, it is more preferred that the radiation energy is electron beams or gamma-rays.

[0029] By the above-mentioned crosslinking treatment, a crosslinked polymer segment is introduced into the polymer, so that a polymer containing a crosslinked polymer segment is obtained. With respect to the shaped porous polymer structure comprising a polymer matrix containing a crosslinked polymer segment formed by the above-mentioned crosslinking treatment, even if the shaped porous polymer structure is immersed in an excess amount of the electrolytic liquid under conditions at which a polymer, if not crosslinked, would be completely dissolved into the electrolytic liquid, dissolution of the whole of the shaped porous polymer structure into the electrolytic liquid does not occur, but only swelling of the shaped porous polymer structure with the electrolytic liquid occurs. The degree of crosslinking of the polymer of the polymer matrix is represented by the gel content, which is obtained from the weight difference of the polymer matrix before and after the extraction-treatment of the polymer matrix with a good solvent for a polymer matrix which is not crosslinked. In this connection, it should be noted that, depending on the conditions at which the shaped porous polymer structure is impregnated and swelled with an electrolytic liquid for producing a hybrid electrolyte, it is possible that the gel content of the polymer matrix of the hybrid electrolyte is different from the gel content of the polymer matrix of the shaped porous polymer structure before being swelled with the electrolytic liquid. Therefore, it is necessary to determine the gel content of the polymer matrix with respect to the polymer matrix obtained from the hybrid electrolyte.

[0030] An example of the method for determining the gel content of a polymer matrix of a hybrid electrolyte is as follows. That is, a produced hybrid electrolyte sheet impregnated and swelled with an electrolytic liquid is immersed in a solvent, which is capable of extracting the electrolytic liquid but not capable of dissolving the polymer matrix, for 30 minutes or more to thereby extraction-remove the impregnated electrolytic liquid from the hybrid electrolyte, followed by drying in vacuum to thereby obtain a dried polymer matrix. The weight (W1) of the dried polymer matrix is measured.

[0031] Then, the dried polymer matrix is wrapped with a stainless steel wire mesh (150-mesh size) and heated in a solvent selected from good solvents for the polymer (before being subjected to crosslinking treatment) as used for producing the hybrid electrolyte for a predetermined period of time under reflux, followed by drying in vacuum, thereby obtaining an extraction residue. The weight (W2) of the extraction residue is measured. The gel content (%) of the polymer matrix is defined as a value obtained by the formula $(W2 / W1) \times 100$. The solvent for the extraction under reflux is used in a weight amount of 100 times or more as large as the weight of the dried polymer matrix. It is preferred that when the polymer (before being subjected to crosslinking treatment) is a vinylidene fluoride polymer, a mixed solvent of N,N-dimethylacetamide (DMAC) and acetone (volume ratio of DMAC to acetone = 7:3) is used as the solvent, and that when the polymer (before being subjected to crosslinking treatment) is an acrylonitrile polymer,

DMAC alone is used as the solvent. Further, in each of these cases, it is preferred that the reflux time is 2 hours or more and the drying is conducted at 70 DEG C for 4 hours or more.

[0032] The shaped porous polymer structure of the hybrid electrolyte of the present invention comprises a polymer matrix having a plurality of cells dispersed therein. Due to such a structure, not only does the hybrid electrolyte comprising a shaped porous polymer structure impregnated and swelled with an electrolytic liquid exhibit a high ionic conductivity, but also the shaped porous polymer structure is advantageously, easily swelled with the electrolytic liquid. The cells may be in the form of closed cells or open cells which form through-holes passing through the shaped porous polymer structure. However, for effectively achieving an easy swelling of the porous polymer structure with an electrolytic liquid, it is preferred that the cells are in the form of open cells which form through-holes passing through the shaped porous polymer structure.

[0033] The void ratio of the shaped porous polymer structure is preferably in the range of from 30 to 95 %. When the void ratio is less than 30 %, the ionic conductivity of the final hybrid electrolyte is unsatisfactory. The void ratio is preferably 40 % or more, more preferably 50 % or more and still more preferably 55 % or more. On the other hand, when the void ratio is more than 95 %, the mechanical strength of the hybrid electrolyte after being swelled with an electrolytic liquid is unsatisfactory. The void ratio is preferably 90 % or less, more preferably 85 % or less and still more preferably 80 % or less.

[0034] Further, it is preferred that the content of the electrolytic liquid in the hybrid electrolyte of the present invention is in the range of from 30 to 95 % by weight, based on the weight of the hybrid electrolyte. When the content of the electrolytic liquid is less than 30 % by weight, the ionic conductivity of the hybrid electrolyte is unsatisfactory. The content of the electrolytic liquid is preferably 40 % by weight or more, more preferably 50 % by weight or more and still more preferably 55 % by weight or more. On the other hand, when the content of the electrolytic liquid is more than 95 % by weight, the mechanical strength of the hybrid electrolyte is unsatisfactory. The content of the electrolytic liquid is preferably 90 % by weight or less, more preferably 85 % by weight or less, still more preferably 80 % by weight or less.

[0035] The void ratio of the shaped porous polymer structure can be obtained by the method comprising filling the voids of the shaped porous polymer structure with a non-solvent for the polymer matrix, followed by determining the weight of the non-solvent filling into the voids. Specifically, when the polymer matrix is produced using, for example, a vinylidene fluoride polymer or an acrylonitrile polymer, the void ratio of the shaped porous polymer structure can be obtained as follows.

[0036] First, the weight (on a dry basis) (A) of a shaped porous polymer structure is measured. Next, the shaped porous polymer structure is immersed in ethanol to thereby render hydrophilic the polymer structure. Subsequently, the resultant hydrophilic polymer structure is immersed in water, thereby replacing the impregnated ethanol by water. The water on the surface of the polymer structure is removed by wiping, and then, the weight (B) of the resultant water-wiped polymer structure is measured. From the weights (A) and (B) obtained above, and the true specific gravity (d) of the material which the shaped porous polymer structure is made of, the void ratio of the shaped porous polymer structure is calculated according to the following formula:

void ratio (%) = $[(B-A)/(A/d + B-A)] \times 100$.

[0037] The form of the hybrid electrolyte of the present invention varies depending on the use thereof. However, when the hybrid electrolyte is sandwiched between the electrodes and used as an electrolyte for the above-mentioned so-called polymer battery, it is preferred that the hybrid electrolyte is in the form of a sheet, a woven fabric, or a nonwoven fabric. In this case, the thickness of the hybrid electrolyte in the form of a sheet is generally in the range of from 1 to 500 μm , preferably from 10 to 300 μm , more preferably from 20 to 150 μm . It is preferred that the shaped porous polymer structure in the form of a sheet, which is used for producing the above-mentioned hybrid electrolyte in the form of a sheet, has a thickness in the same range as mentioned above. When the thickness of the hybrid electrolyte or shaped porous polymer structure in the form of a sheet is less than 1 μm , the mechanical strength of hybrid electrolyte or shaped porous polymer structure is unsatisfactory. Further, when such a hybrid electrolyte is laminated onto an electrode to thereby obtain a battery, a short-circuiting of the obtained battery between the electrodes is likely to occur. On the other hand, when the thickness of the hybrid electrolyte or shaped porous polymer structure in the form of a sheet is more than 500 μm , the effective electric resistance as a hybrid electrolyte is disadvantageously high and, for example, when such a hybrid electrolyte is used as an electrolyte for a polymer battery, the energy density per volume is extremely low.

[0038] There is no particular limitation with respect to the methods for producing the shaped porous polymer

structure used in the present invention. As a method for producing a shaped porous polymer structure comprising open cells which form through-holes passing through the shaped porous polymer structure, a conventional method for producing a microfilter or ultrafilter can be employed. Examples of such methods include the methods described in Unexamined Japanese Patent Application Laid-Open Specification No. 3-215535, Examined Japanese Patent Application Publication No. 61-38207 and Unexamined Japanese Patent Application Laid-Open Specification No. 54-16382. Examples of such methods include the fusing method and the wet method. The fusing method is a method for producing a shaped porous polymer structure in the form of a sheet, which comprises fusing a polymer together with a plasticizer, an inorganic particulate and the like to thereby obtain a fused polymer; shaping the obtained fused polymer into a sheet to thereby obtain a shaped polymer structure in the form of a sheet; and extraction-removing the plasticizer, the inorganic particulate and the like contained in the shaped polymer structure to thereby obtain a desired shaped porous polymer structure. On the other hand, the wet method is another method for producing a shaped porous polymer structure in the form of a sheet, which comprises dissolving a polymer into a solvent together with a surfactant, an additive and the like to thereby obtain a solution; casting the obtained solution into a liquid film; and immersing the liquid film in a non-solvent for the polymer so as to solidify the film and so as to remove the solvent, surfactant, additive and the like contained in the liquid film, to thereby obtain a desired shaped porous polymer structure.

[0039] Further, examples of methods for producing a shaped porous polymer structure containing closed cells include a method comprising shaping a polymer containing a foaming agent to obtain a shaped structure having dispersed therein the foaming agent; and heating the shaped structure or holding the shaped structure under reduced pressure so as to form closed cells in the shaped structure, thereby obtaining a shaped porous polymer structure comprising the closed cells. As a method for producing the shaped porous polymer structure of the present invention, the above-mentioned methods can be used individually or in combination.

[0040] In the present invention, there is no particular limitation with respect to the method for swelling a shaped porous polymer structure with an electrolyte so as to produce the hybrid electrolyte of the present invention. There can be mentioned a method comprising holding an impregnated, shaped porous polymer structure (i.e., a shaped porous polymer structure which is impregnated with an electrolytic liquid, wherein the electrolytic liquid is used in an amount sufficient to swell the shaped porous polymer structure) under predetermined swelling temperature and pressure conditions at which the shaped porous polymer structure is susceptible to swelling with the electrolytic liquid, to thereby swell the porous polymer structure. After the swelling, the swelled, shaped porous polymer structure may or may not exhibit dimensional change. The expression "the shaped porous polymer structure does not exhibit dimensional change" means that the shaped porous polymer structure before impregnation with an electrolytic liquid is substantially identical in size with the hybrid electrolyte produced using the shaped polymer structure, but the shaped porous polymer structure in the hybrid electrolyte is in a swollen state as defined above. That is, even if the shaped porous polymer structure does not exhibit any dimensional change after swelling, the degree of shrinkage of the shaped porous polymer structure of the hybrid electrolyte of the present invention is more than 10 %, wherein the degree of shrinkage of the shaped porous polymer structure is defined as the change in the longitudinal length of the dried polymer matrix (i.e., the shaped porous polymer structure obtained by removing the impregnated electrolytic liquid from the hybrid electrolyte, followed by drying in vacuum), relative to the longitudinal length of the electrolytic liquid-impregnated hybrid electrolyte.

[0041] Further, as mentioned above, the gel content of the polymer matrix of the hybrid electrolyte of the present invention must be within the above-mentioned specific range. Depending on the method of swelling a shaped porous polymer structure with an electrolytic liquid for producing a hybrid electrolyte, it is possible that a portion of the polymer matrix is dissolved in the electrolytic liquid, so that the gel content of the polymer matrix remaining undissolved becomes higher than the above-mentioned specific range. However, when a shaped porous polymer structure is swelled with an electrolytic liquid by an appropriate method, such as a method in which the electrolytic liquid is used in an amount insufficient to unrestrictedly swell the shaped porous polymer structure (i.e. in an amount such that the swelling of the shaped porous polymer structure cannot reach the equilibrium of swelling), or a method in which the temperature and time for swelling the shaped porous polymer structure with the electrolytic liquid is controlled, the dissolution of a portion of the polymer matrix in the electrolytic liquid during the immersion of the shaped porous polymer structure in the electrolytic liquid is prevented, so that the gel content of the polymer matrix can be maintained at a level within the above-mentioned specific range. By such methods, the hybrid electrolyte of the present invention can be produced.

[0042] Alternatively, the hybrid electrolyte of the present invention can be effectively produced by the following method. That is, first, a shaped porous polymer structure is impregnated with an electrolytic liquid under predetermined non-swelling temperature and pressure conditions at which the shaped porous polymer

structure is substantially insusceptible to swelling with the electrolytic liquid, thereby obtaining an impregnated, shaped porous polymer structure. In general, as a method for impregnating the shaped porous polymer structure, there can be mentioned a method wherein the shaped porous polymer structure is immersed in an electrolytic liquid bath. As another method for impregnating the shaped porous polymer structure, there can be mentioned a method in which the electrolytic liquid is applied to the shaped porous polymer structure by spraying or coating. The impregnated, shaped porous polymer structure obtained by the above methods is still not swelled with the electrolytic liquid, so that the shaped porous polymer structure has a satisfactorily high mechanical strength and that a dimensional change of the shaped porous polymer structure does almost not occur. Therefore, at this stage of only impregnation, the handling of the shaped porous polymer structure is relatively easy.

[0043] Next, the shaped porous polymer structure in the above-mentioned state is taken out of the impregnating device, such as the electrolytic liquid bath, the spraying device, the coating device or the like. The excess electrolytic liquid on the shaped porous polymer structure flows down so as to be removed from the polymer structure. If desired, the excess electrolytic liquid is removed by an appropriate method, such as shaking off, wiping out or the like.

[0044] On the other hand, in the present invention, a method can be employed in which the shaped porous polymer structure may be laminated to an electrode to thereby obtain a laminate structure, and the laminate structure is impregnated with the electrolytic liquid under predetermined non-swelling temperature and pressure conditions at which the shaped porous polymer structure is substantially insusceptible to swelling with the electrolytic liquid, to thereby obtain an impregnated laminate structure. The excess electrolytic liquid on the obtained impregnated laminate structure is removed in substantially the same manner as mentioned above.

[0045] The ionic conductivity of the impregnated, shaped porous polymer structure in the above-mentioned non-swollen state is not satisfactorily high. However, when the impregnated, shaped porous polymer structure as such, or the impregnated laminate structure (wherein the impregnated shaped porous polymer structure is laminated to an electrode) is held under predetermined swelling temperature and pressure conditions at which the shaped porous polymer structure is susceptible to swelling with the electrolytic liquid, to thereby swell the shaped porous polymer structure with the electrolytic liquid, a hybrid electrolyte having a high ionic conductivity of the present invention can be easily obtained. Especially when the impregnated, shaped porous polymer structure is laminated to an electrode and the resultant laminate structure is heated for swelling, the improvement of the ionic conductivity and the adhesion of the resultant hybrid electrolyte to the electrode can be simultaneously achieved.

[0046] Further, when the above-mentioned "impregnating and swelling" method of the present invention is employed, it becomes possible to prevent the dissolution of a portion of the polymer matrix into the electrolytic liquid, so that the electrolytic liquid bath or the like is free from dusty substances derived from a portion of the polymer matrix which is dissolved in the electrolytic liquid.

[0047] As described above, in general, when a crosslinked polymer is unrestrictedly swelled in a solvent or solution, the crosslinked polymer is swelled, with a great dimensional change, until the swelling of the crosslinked polymer reaches the equilibrium of swelling. It is extremely difficult to control, in order to prevent the dimensional change of the crosslinked polymer, the quantity of the solvent or solution entering the crosslinked polymer for the swelling of the crosslinked polymer so that the swelling of the crosslinked polymer does not reach the equilibrium of swelling. However, when a shaped porous polymer structure is swelled with an electrolytic liquid by the above-mentioned "impregnating and swelling" method, the void ratio of the shaped porous polymer structure functions to provide a limitation with respect to the quantity of the electrolytic liquid entering the shaped porous polymer structure for the swelling of the shaped porous polymer structure, so that the degree of swelling of the shaped porous polymer structure is also limited. Accordingly, the great dimensional change and lowering of the mechanical strength of the shaped porous polymer structure due to the swelling do not occur. Therefore, especially when the shaped porous polymer structure (which may be either impregnated or not impregnated with an electrolytic liquid as described below) is laminated to an electrode before the shaped porous polymer structure is swelled with an electrolytic liquid, the above-mentioned "impregnating and swelling" method is advantageous in that not only can a shaped porous polymer structure having a high mechanical strength be laminated to an electrode, but also the dimensional change of the shaped porous polymer structure due to the swelling can be suppressed.

[0048] The swelling is generally conducted under atmospheric pressure, but, if desired, it may be conducted under reduced pressure or superatmospheric pressure. The electrolytic liquid may or may not remain in the cells of the hybrid electrolyte after the swelling (the cells are those which are derived from the cells of the

shaped porous polymer structure). However, it is preferred that the hybrid electrolyte contains a liquid phase, especially a liquid phase passing through the hybrid electrolyte.

[0049] Thus, in a further aspect of the present invention, there is provided a method for producing an electrochemical device, which comprises:

impregnating a shaped porous polymer structure, which comprises a polymer matrix and a plurality of cells dispersed in the polymer matrix, wherein the polymer matrix contains a crosslinked polymer segment, with an electrolytic liquid selected from the group consisting of a solution of an electrolyte in water or a non-aqueous solvent and a liquid electrolyte under predetermined non-swelling temperature and pressure conditions at which the shaped porous polymer structure is substantially insusceptible to swelling with the electrolytic liquid, thereby obtaining an impregnated, shaped porous polymer structure;
laminating the impregnated, shaped porous polymer structure to an electrode to thereby obtain a laminate structure; and
holding the laminate structure under predetermined swelling temperature and pressure conditions at which the shaped porous polymer structure is susceptible to swelling with the electrolytic liquid.

[0050] In still a further aspect of the present invention, there is provided a method for producing an electrochemical device, which comprises:

laminating a shaped porous polymer structure, which comprises a polymer matrix and a plurality of cells dispersed in the polymer matrix, wherein the polymer matrix contains a crosslinked polymer segment, to an electrode to thereby obtain a laminate structure;
impregnating the laminate structure with an electrolytic liquid selected from the group consisting of a solution of an electrolyte in water or a non-aqueous solvent and a liquid electrolyte under predetermined non-swelling temperature and pressure conditions at which the shaped porous polymer structure is substantially insusceptible to swelling with the electrolytic liquid, thereby obtaining an impregnated laminate structure; and
holding the impregnated laminate structure under predetermined swelling temperature and pressure conditions at which the shaped porous polymer structure is susceptible to swelling with the electrolytic liquid.

[0051] In the present invention, the "swelling temperature and pressure conditions at which the shaped porous polymer structure is susceptible to swelling with the electrolytic liquid" are the temperature and pressure conditions at which the change (%) in the longitudinal length of the shaped porous polymer structure, which is determined after immersing the shaped porous polymer structure in an electrolytic liquid under predetermined temperature and pressure conditions, relative to the longitudinal length measured before the immersion, is more than 10 %. Therefore, the susceptibility of the shaped porous polymer structure to swelling with the electrolytic liquid (under predetermined temperature and pressure conditions) can be confirmed from the occurrence of dimensional change of the shaped porous polymer structure at the immersion of the shaped porous polymer structure in the electrolytic liquid under the predetermined temperature and pressure conditions. However, with respect to the above-mentioned method (i.e., a method which comprises impregnating a shaped porous polymer structure with an electrolytic liquid under predetermined non-swelling temperature and pressure conditions at which the shaped porous polymer structure is substantially insusceptible to swelling with the electrolytic liquid, thereby obtaining an impregnated, shaped porous polymer structure; removing the excess electrolytic liquid on the obtained impregnated, shaped porous polymer structure; laminating the impregnated, shaped porous polymer structure to an electrode to thereby obtain a laminate structure; and holding the laminate structure under predetermined swelling temperature and pressure conditions at which the shaped porous polymer structure is susceptible to swelling with the electrolytic liquid, so that the shaped porous polymer structure is swelled with the electrolytic liquid), the size of the shaped porous polymer structure which is swelled with the electrolytic liquid is substantially the same as the size of the shaped porous polymer structure which is not swelled with the electrolytic liquid. Therefore, the susceptibility of the shaped porous polymer structure to swelling with the electrolytic liquid cannot be confirmed directly from an occurrence of dimensional change of the shaped porous polymer structure in the middle of the above-mentioned method, and it is necessary to separately confirm the swelling temperature and pressure conditions at which the shaped porous polymer structure is susceptible to swelling with the electrolytic liquid, with respect to the shaped porous polymer structure in a non-laminated form.

[0052] Further, in the present invention, the "non-swelling temperature and pressure conditions at which the shaped porous polymer structure is substantially insusceptible to swelling with the electrolytic liquid" are the temperature and pressure conditions at which the change (%) in the longitudinal length of the shaped porous polymer structure, which is determined after immersing the shaped porous polymer structure in the electrolytic

liquid under predetermined temperature and pressure conditions, relative to the longitudinal length measured before the immersion, is 10 % or less, or the temperature and pressure conditions at which the degree of shrinkage (%) of the shaped porous polymer structure [which is defined as the change in the longitudinal length of the dried polymer matrix (i.e., the shaped porous polymer structure obtained by extraction-removing the impregnated electrolytic liquid from the hybrid electrolyte (which is obtained by immersing the shaped porous polymer matrix in the electrolytic liquid under predetermined temperature and pressure conditions), followed by drying at room temperature)], relative to the longitudinal length of the electrolytic liquid-impregnated hybrid electrolyte, is 10 % or less.

[0053] The type of polymer for use in producing the hybrid electrolyte of the present invention varies depending on the type of the electrolytic liquid used. Conversely, the type of hydrolytic liquid for use in producing the hybrid electrolyte of the present invention varies depending on the type of the polymer used. The electrolytic liquid contained in the hybrid electrolyte of the present invention is selected from the group consisting of a solution of an electrolyte in water or a non-aqueous solvent and a liquid electrolyte. Examples of electrolytic liquids are described below. The electrolyte used in the form of a solution in water or a non-aqueous solvent may be an inorganic or organic salt or an inorganic or organic acid. Examples of electrolytes include inorganic acids, such as tetrafluoroboric acid, hexafluorophosphoric acid, perchloric acid, hexafluoroarsenic acid, nitric acid, sulfuric acid, phosphoric acid, hydrofluoric acid, hydrochloric acid, hydrobromic acid, hydroiodic acid and the like; organic acids, such as trifluoromethanesulfonic acid, heptafluoropropylsulfonic acid, bis(trifluoromethanesulfonyl)imide acid, acetic acid, trifluoroacetic acid, propionic acid and the like; and salts of these inorganic and organic acids. Further, the above-mentioned acids and salts can be used individually or in combination. Examples of cations for the above-mentioned electrolytic salts include an alkali metal, an alkaline earth metal, a transition metal, a rare earth metal, an ammonium ion and the like. The above-mentioned cations can be used individually or in combination. The preferred cation species varies depending on the use of the hybrid electrolyte. For example, when the hybrid electrolyte of the present invention is used in a lithium battery, it is preferred to use a lithium salt as an electrolyte. Especially when the hybrid electrolyte of the present invention is used in a lithium secondary battery, in which a wide range of electrochemical window is utilized, it is preferred that the electrolyte is an electrochemically stable lithium salt. Examples of such lithium salts include a lithium salt of fluoroalkylsulfonic acid, such as CF₃SO₃Li and C₄F₉SO₃Li; and a lithium salt of sulfonimide, such as (CF₃SO₂)₂NLi; LiBF₄, LiPF₆, LiClO₄ and LiAsF₆. The appropriate concentration of the electrolyte in a solution varies depending on the use of the hybrid electrolyte. However, it is generally in the range of from 0.1 mol/liter to the saturation solubility, preferably in the range of from 0.5 to 5 mol/liter, more preferably in the range of from 0.5 to 2 mol/liter.

[0054] As a solvent for dissolving the above-mentioned electrolyte, there can be mentioned chemically stable solvents in which the above-mentioned electrolyte can be dissolved, such as water, alcohol and the like. When the hybrid electrolyte of the present invention is used in an electrochemical device containing a non-aqueous electrolytic liquid, such as a lithium battery, examples of solvents include carbonate compounds, such as ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, methyl ethyl carbonate and the like; ether compounds, such as tetrahydrofuran, dimethoxyethane, diglyme, tetraglyme, oligoethylene oxide and the like; lactone compounds, such as gamma -butyrolactone, beta -propiolactone and the like; and nitrile compounds, such as acetonitrile, propionitrile and the like.

[0055] Among the above-mentioned polymers and electrolytic liquids, an appropriate combination of a polymer and an electrolytic liquid is employed, wherein the shaped porous polymer structure produced using the polymer is swelled with the electrolytic liquid. It is preferred that the shaped porous polymer structure produced using the polymer is susceptible to swelling with the electrolytic liquid (a solution of an electrolyte) at a temperature which is lower than the boiling point of the solvent for dissolving the electrolyte. It is especially preferred that the shaped porous polymer structure produced using the polymer is susceptible to swelling with the electrolytic liquid (a solution of an electrolyte) at a temperature which is lower than the boiling point of the solvent for dissolving the electrolyte, but the shaped porous polymer structure is substantially insusceptible to swelling with the electrolytic liquid at room temperature. As examples of such combinations, there can be mentioned a combination of a carbonate solvent, such as ethylene carbonate and propylene carbonate, as a solvent for the electrolyte and a vinylidene fluoride polymer (i.e., polyvinylidene fluoride and a copolymer of vinylidene fluoride), or polyacrylonitrile as a polymer. When the above combination of a solvent and a polymer is employed, the impregnation is preferably conducted at the temperature of 35 DEG C or less and the swelling is preferably conducted at the temperature of 80 DEG C or more, more preferably 90 DEG C or more.

[0056] In the present invention, it is required that the shaped porous polymer structure be finally swelled with the electrolytic liquid. Whether or not the shaped porous polymer structure is susceptible to swelling with the

electrolytic liquid under a certain pressure depends on the temperature. That is, the shaped porous polymer structure is substantially insusceptible to swelling with the electrolytic liquid under a certain temperature. Practically, it is preferred that the non-swelling temperature and pressure conditions at which the shaped porous polymer structure is substantially insusceptible to swelling are the conditions of approximately room temperature and approximately atmospheric pressure. Incidentally, whether or not the shaped porous polymer structure is susceptible to swelling with the electrolytic liquid depends also on the time of contacting the shaped porous polymer structure with the electrolytic liquid. However, when almost no change in size of the shaped porous polymer structure occurs even after immersing the shaped porous polymer structure in the electrolytic liquid for approximately one hour at a predetermined temperature under atmospheric pressure, the shaped porous polymer structure is regarded to be substantially insusceptible to swelling with the electrolytic liquid at the predetermined temperature.

[0057] On the other hand, the susceptibility of the shaped porous polymer structure to swelling with the electrolytic liquid at a predetermined temperature can be confirmed from the occurrence of dimensional change of the shaped porous polymer structure at the immersion of the shaped porous polymer structure in the electrolytic liquid at the predetermined temperature. That is, when the shaped porous polymer structure is swelled with the electrolytic liquid by heating under a certain pressure, the lowest temperature required for swelling the shaped porous polymer structure varies depending on the types of the polymer and the electrolytic liquid which are used in combination. The lowest temperature can generally be determined by measuring the temperature at which the dimensional change of the shaped porous polymer structure occurs when the shaped porous polymer structure is immersed in the electrolytic liquid. However, when the shaped porous polymer structure is laminated to an electrode, it is difficult to know whether or not the dimensional change of the shaped porous polymer structure has occurred. Therefore, it is preferred to separately determine the lowest temperature required for swelling, with respect to the shaped porous polymer structure in a non-laminated form. The lowest temperature required for swelling is preferably higher than room temperature, more preferably not less than 20 DEG C higher than room temperature, and lower than the boiling point of the solvent used for the electrolytic liquid. Further, when the shaped porous polymer structure is heated so as to be swelled with an electrolytic liquid after the shaped porous polymer structure is laminated to an electrode, the lowest temperature required for swelling is preferably lower than the temperature at which the electrode activity of an electrode material used for the electrode begins to deteriorate. The time of heating required for swelling varies depending on the temperature for swelling and the mode of heating and, therefore, cannot be simply determined. However, the heat-ing is conducted generally for 2 minutes or more, preferably 10 minutes or more, more preferably 30 minutes or more. When the temperature for swelling is satisfactorily higher than the lowest temperature required for swelling, about 2 minutes of heating is sufficient for swelling.

[0058] As mentioned above, as methods for producing an electrochemical device, such as a battery, in which the hybrid electrolyte of the present invention is contained, there can be mentioned the following two methods, i.e., a method which comprises impregnating a shaped porous polymer structure with an electrolytic liquid, thereby obtaining an impregnated, shaped porous polymer structure; laminating the impregnated, shaped porous polymer structure to an electrode to thereby obtain a laminate structure; and heating the laminate structure, and a method which comprises laminating a shaped porous polymer structure to an electrode to thereby obtain a laminate structure; impregnating the laminate structure with an electrolytic liquid, thereby obtaining an impregnated laminate structure; and heating the impregnated laminate structure. With respect to the latter method, when an electrode having a current collector is used for producing an electrochemical device, the laminate structure can be effectively impregnated with the electrolytic liquid by using, as the current collector, a mesh current collector. Examples of morphologies of the laminate structures include a sheet form, a roll form, a folding sheet form, a laminate form and the like.

[0059] In the method of the present invention for producing an electrochemical device, the material for an electrode varies depending on the type of the electrochemical device to be produced. For example, when the electrochemical device is a lithium battery, a substance capable of occluding and releasing lithium is used as a material for the positive electrode and negative electrode. As the positive electrode material, a material having a higher electric potential than that of the negative electrode is selected. Examples of such positive electrode materials include oxides, such as $\text{Li}_1\text{-XCoO}_2$, $\text{Li}_1\text{-XNiO}_2$, $\text{Li}_1\text{-XMn}_2\text{O}_4$, $\text{Li}_1\text{-XMO}_2$ (wherein 0 [0060] As the negative electrode material, a material having a lower electric potential than that of the positive electrode is employed. Examples of negative electrode materials include metallic lithium-containing materials, such as metallic lithium, an aluminum-lithium alloy and a magnesium-aluminum-lithium alloy; carbonaceous materials, such as a graphite, a coke, a low temperature-calcined polymer; lithium solid solutions of metal oxides, such as an SnM oxide (wherein M represents Si, Ge or Pb), a complex oxide of $\text{Si}_1\text{-YM'YOZ}$ oxide (wherein M' represents W, Sn, Pb, B or the like), a titanium oxide and an iron oxide; and ceramics, such as nitrides, e.g., Li_7MnN_4 , Li_3FeN_2 , $\text{Li}_3\text{-XCoXN}$, $\text{Li}_3\text{-XNiN}$, $\text{Li}_3\text{-XCuXN}$, Li_3BN_2 , Li_3AlN_2 and Li_3SiN_3 . It should

be noted that when metallic lithium formed on the negative electrode by the reduction of lithium ions on the negative electrode is used as a negative electrode material, the type of the material for the negative electrode is not particularly limited as long as it is electrically conductive.

[0061] The positive and negative electrodes are produced by molding the above-mentioned materials into predetermined morphologies. The electrode may be either in the form of a continuous solid or in the form of a particulate electrode material dispersed in a binder. Examples of methods for forming a continuous solid include electrolysis, vacuum deposition, sputtering, CVD, melt processing, sintering and compression. In a method for forming a particulate electrode material dispersed in a binder, an electrode is produced by molding a mixture of a particulate electrode material and a binder. Examples of binders include an ionic conductive polymer, such as polyvinylidene fluoride; a non-ionic conductive polymer, such as a styrene-butadiene latex and Teflon latex; and metals. A polymerizable monomer and a crosslinking agent may be added to the binder, and the resultant mixture may be subjected to molding, followed by polymerization and crosslinking. For the purpose of improving the binding strength of such a binder or modifying the properties of such a binder, the binder may be irradiated with radiant energy, such as electron beams, gamma -rays, ultraviolet rays and infrared rays. For effecting ion transportation between the positive and negative electrodes, current collectors made of a material having low electrical resistance may be provided on the positive and negative electrodes. In producing an electrode according to the above-mentioned methods, the current collector is used as a substrate for the electrode.

[0062] When a shaped porous polymer structure is laminated to an electrode, the electrode can be impregnated with an electrolytic liquid in advance. When a laminate structure comprising an impregnated, shaped porous polymer structure or a hybrid electrolyte and an electrode is heated in the presence of the electrolytic liquid used for impregnating the electrode, the adherence strength of the impregnated, shaped porous polymer structure or the hybrid electrolyte to the electrode is remarkably improved.

[0063] Examples of electrochemical devices comprising the hybrid electrolyte of the present invention include primary and secondary batteries (e.g., a lithium battery), a photoelectrochemical device and an electrochemical sensor.

[0064] As mentioned above, the hybrid electrolyte of the present invention has a high ionic conductivity, an excellent high temperature stability and an excellent adherability to an electrode. Further, when the method of the present invention is employed for producing a hybrid electrolyte or an electrochemical device, during the course of the production of the hybrid electrolyte or the electrochemical device, not only is the strength of an impregnated, shaped porous polymer structure extremely high, but also the dimensional change of the shaped porous polymer structure swelled with an electrolytic liquid, relative to the shaped porous polymer structure which is not swelled, is advantageously suppressed. Therefore, it becomes possible to effectively produce not only a hybrid electrolyte having the above-mentioned excellent properties, but also a high performance electrochemical device. Further, the method of the present invention is very advantageous from an industrial point of view in that, in practicing the method of the present invention, a dissolution of a portion of the polymer matrix into an electrolytic liquid does not occur and, therefore, the impregnation apparatus, such as an electrolyte liquid bath, is free from dusty substances derived from a portion of the polymer matrix which is dissolved in the electrolytic liquid. The hybrid electrolyte of the present invention is especially useful as an electrolyte for the so-called polymer batteries.

BEST MODE FOR CARRYING OUT THE INVENTION

[0065] The present invention will be described in more detail with reference to Examples and Comparative Examples, which should not be construed as limiting the scope of the present invention.

[0066] In the Examples and Comparative Examples, the measurement of the void ratio of a shaped porous polymer structure, the measurement of the degree of shrinkage of a shaped porous polymer structure, the measurement of the gel content of a polymer matrix, and the evaluation of the ionic conductivity were performed by the following methods.

(i) Measurement of the void ratio of a shaped porous polymer structure

[0067] First, the weight on a dry basis (A) of a shaped porous polymer structure was determined. Next, the

shaped porous polymer structure was immersed in ethanol to thereby render hydrophilic the polymer structure. Subsequently, the resultant hydrophilic polymer structure was immersed in water, thereby replacing the impregnated ethanol by water. The water on the surface of the polymer structure was removed by wiping, and then, the weight (B) of the resultant water-wiped polymer structure was measured. From the weights (A) and (B) obtained above and the true specific gravity (d) of the material which the shaped porous polymer structure is made of, the void ratio of the shaped porous polymer structure was calculated according to the following formula:

$$\text{void ratio (\%)} = [(B-A)/(A/d + B-A)] \times 100.$$

(ii) Measurement of the degree of shrinkage of a shaped porous polymer structure and measurement of the gel content of a polymer matrix

[0068] From a produced hybrid electrolyte sheet impregnated with an electrolytic liquid was cut out a sample having a predetermined size, and the sample was immersed in ethanol for 30 minutes or more to thereby extraction-remove the impregnated electrolytic liquid from the sample, followed by drying in vacuum to thereby obtain a dried polymer matrix. The weight of the dried polymer matrix was measured.

[0069] In this instance, the degree of shrinkage of the shaped porous polymer structure of the hybrid electrolyte was determined. That is, the change in the longitudinal length of the above-obtained dried polymer matrix (shaped porous polymer structure), relative to the longitudinal length of the electrolytic liquid-impregnated hybrid electrolyte sheet, was determined. This change (%) is defined as the degree of shrinkage of the shaped porous polymer structure.

[0070] The weight of the above-obtained dried polymer matrix was measured. Then, the dried polymer matrix was wrapped with a stainless steel wire mesh (150-mesh size) and heated in a solvent for 4 hours under reflux, wherein the solvent was used in a weight amount of not less than 1000 times the weight of the dried polymer matrix. As the solvent, a mixed solvent of N,N-dimethylacetamide (DMAC) and acetone (volume ratio of DMAC to acetone = 7:3) was used for a vinylidene fluoride polymer matrix, and DMAC alone was used for an acrylonitrile polymer matrix. Subsequently, the resultant polymer matrix was subjected to extraction with acetone for 5 minutes, followed by drying in vacuum at 70 DEG C, thereby obtaining an extraction residue. The weight of the extraction residue was measured. The gel content of the polymer matrix was defined as a value obtained by dividing the weight of the extraction residue by the weight of the dried polymer matrix.

(iii) Evaluation of the ionic conductivity

[0071] A sample (an impregnated porous polymer sheet, or a hybrid electrolyte, i.e., a swollen form of an impregnated porous polymer sheet) was sandwiched between two electrode sheets to thereby obtain an electrochemical cell. An alternating voltage was applied between the electrodes, and the complex impedance was measured by alternating-current impedance method. In accordance with a conventional method, the ionic conductivity of the sample was calculated from the real part of the obtained complex impedance expressed in the form of a Cole-Cole plot, the thickness of the sample, and the surface areas of the electrodes.

Example 1

&lang&Production of a hybrid electrolyte&rang&

[0072] A solution consisting of 17.3 parts by weight of a hexafluoropropylene/vinylidene fluoride copolymer resin (hexafluoropropylene content: 5 % by weight), 11.5 parts by weight of polyethylene glycol (average molecular weight: 200) and 71.2 parts by weight of dimethylacetamide was prepared, and to 100 g of the thus prepared solution was added 0.8 ml of polyoxyethylene sorbitane monooleate (Trade name: Tween 80, manufactured and sold by Kao Atlas K.K., Japan), thereby obtaining a homogeneous solution. The obtained homogeneous solution was cast on a glass plate at room temperature, thereby preparing a liquid film having a thickness of 200 μ m. Immediately, the prepared liquid film was immersed in water at 70 DEG C to thereby

solidify the film, and then, the solidified film was washed with water and alcohol, followed by drying, thereby obtaining a porous polymer sheet having a thickness of 52 μm and a void ratio of 76 %. The prepared porous polymer sheet was irradiated with electron beams (irradiation dose: 15 Mrads) to thereby prepare a crosslinked porous polymer sheet.

[0073] An electrolytic liquid was obtained by dissolving lithium tetrafluoroborate (LiBF_4) in a mixed solvent of ethylene carbonate (EC) and propylene carbonate (PC) (EC/PC weight ratio = 1/1, and LiBF_4 concentration: 1 mol/liter), and the crosslinked porous polymer sheet prepared above was immersed in the above-obtained electrolytic liquid at room temperature. When the crosslinked porous polymer sheet was immersed in the electrolytic liquid, the sheet was immediately impregnated with the electrolytic liquid, and an impregnated transparent porous polymer sheet was obtained with ease. The electrolytic liquid on the surface of the impregnated porous polymer sheet (that is, an excess electrolytic liquid which did not impregnate the porous polymer sheet) was removed by wiping the porous polymer sheet. The change in the size of the impregnated porous polymer sheet was 5 % in the longitudinal direction of the sheet, relative to the size of the non-impregnated porous polymer sheet. The impregnated porous polymer sheet was sandwiched between two glass plates and heated at 100 DEG C in an oven for 2 hours, to thereby obtain a hybrid electrolyte sheet. No change in the size of the impregnated porous polymer sheet was observed between the impregnated porous polymer sheet before the heat treatment and the hybrid electrolyte sheet obtained after the heat treatment. From the obtained hybrid electrolyte sheet was cut out a sample having a predetermined size, and the electrolytic liquid was removed by extraction, followed by drying, to thereby obtain a dried polymer matrix. The degree of shrinkage of the porous polymer sheet was 16 %, as calculated from the size of the dried polymer matrix and the size of the hybrid electrolyte sheet, and the gel content of the polymer matrix was 62 %. On the other hand, when the above-obtained crosslinked porous polymer sheet was immersed in the electrolytic liquid at 100 DEG C for 1 hour, the size of the porous polymer sheet increased by 36 % in the longitudinal direction of the sheet, based on the size of the porous polymer sheet before the immersion in the electrolytic liquid. Thus, the above-mentioned temperature was confirmed to be a temperature at which the porous polymer sheet can be swelled with the electrolytic liquid.

[0074] A sample of the obtained hybrid electrolyte sheet was sandwiched between two stainless steel sheets, thereby obtaining an electrochemical cell. The obtained electrochemical cell was subjected to a measurement of an alternating-current impedance, using the above-mentioned two stainless steel sheets as electrodes. (The alternating-current impedance was measured by means of impedance measurement apparatus Model 398 manufactured and sold by Seiko EG&G, Japan). As a result, it was found that the ionic conductivity of the hybrid electrolyte sheet at room temperature was 1.3 mS/cm.

&lang&Production of a battery&rang&

[0075] A powder of lithium cobalt oxide (LiCoO_2 ; average particle diameter: 10 μm) and carbon black were added to and dispersed in a 5 % by weight solution of polyvinylidene fluoride (KF1100, manufactured and sold by Kureha Chemical Industry Co., Ltd., Japan) in N-methylpyrrolidone (NMP), so that a slurry containing solid components in the following weight ratio was obtained: LiCoO_2 (85 %), carbon black (8 %) and polyvinylidene fluoride (7 %). The obtained slurry was applied onto an aluminum foil (as a current collector) by doctor blade method and dried, to thereby prepare an electrode layer having a thickness of 110 μm . The prepared electrode layer on the aluminum sheet was used as an LiCoO_2 electrode sheet (positive electrode).

[0076] A powder of needle coke (NC) having an average particle diameter of 10 μm was homogeneously mixed with the above-mentioned 5 % by weight solution of polyvinylidene fluoride in N-methylpyrrolidone (NMP), thereby obtaining a slurry (NC/polymer dry weight ratio = 92:8). The obtained slurry was applied onto a copper sheet (as a current collector) by doctor blade method and dried, to thereby prepare an electrode layer having a thickness of 120 μm . The prepared electrode layer on the copper sheet was used as a needle coke electrode sheet (negative electrode).

[0077] From the LiCoO_2 electrode sheet and the needle coke electrode sheet were individually cut out a sample having a size of 4 cm x 4 cm, and the obtained samples were impregnated with the electrolytic liquid mentioned above. From an impregnated porous polymer sheet, obtained by immersing the crosslinked porous polymer sheet in the above-mentioned electrolytic liquid at room temperature, was cut out a sample having a size of 4.5 cm x 4.5 cm, and the sample of the impregnated porous polymer sheet was sandwiched between the above-prepared electrode sheets so as to obtain a laminate structure (when preparing the laminate structure, both sides of the impregnated porous polymer sheet were respectively, securely attached to the electrode layers of the two electrode sheets), thereby preparing a battery composed of a negative electrode

(needle cokes), an impregnated porous polymer sheet, and a positive electrode (LiCoO_2). The prepared battery was further sandwiched between two glass plates and held by means of a clip. Then, the resultant structure was heated at 100 DEG C for 2 hours, followed by cooling to room temperature, and the glass plates were removed from the battery. Stainless steel sheets (as electric terminals for taking a current) were brought into contact with the respective current collectors of the positive and negative electrodes of the battery, and the battery was placed between two opposite PET/Al/PE laminate films (PET: polyethylene terephthalate film, Al: aluminum sheet, PE: polyethylene film) so that the current collectors project from the resultant structure. The laminate structure of the resultant structure was made secure by means of a laminator, to thereby obtain a sheet battery.

[0078] The electric terminals of the obtained sheet battery were connected to a charge/discharge testing device (Model 101SM, manufactured and sold by Hokuto Denko Corporation, Japan), and the battery was subjected to charge/discharge cycle testing at a current density of 1 mA/cm. The charging operation was conducted at a constant potential of 4.2 V. After the charging operation, the potential between the electrodes was 4.2 V. The discharging operation was conducted at a constant current, and discontinued when the electric potential was decreased to 2.7 V. As a result of the charge/discharge testing, it was found that the discharge/charge efficiency (ratio) at the first cycle was 80 % or more, and with respect to the cycles after the first cycle, each of the discharge/charge efficiencies (ratio) was 99 % or more. These results show that this battery is capable of being repeatedly charged and discharged and hence operable as a secondary battery.

[0079] After repeating the charge/discharge testing ten cycles, both of the two opposite PET/Al/PE laminate films were removed from the sheet battery, thereby isolating the battery. An attempt was made to remove the electrode sheets from the isolated battery; however, only the current collectors (metal sheets) came off the battery, thus demonstrating that the electrode sheets are securely attached to both sides of the electrolyte sheet. In this situation, after removing the current collectors from the battery, the electrolyte layer of the battery, together with the electrode layers, was washed with ethanol, followed by an extraction of the electrolytic liquid. Then, a major portion of each of the electrode layers on both surfaces of the electrolyte layer was scraped off, thereby obtaining a polymer sheet. Further, the obtained polymer sheet was dried to thereby obtain a sheet of dried polymer matrix. The degree of shrinkage of the porous polymer sheet after drying was 12 % and the gel content of the dried polymer matrix was 64 %.

Comparative Example 1

[0080] From substantially the same porous polymer sheet as prepared in Example 1 was cut out a sample having a size of 4 cm x 4 cm. Without subjecting the sample to irradiation, the sample was immersed in an electrolytic liquid which is substantially the same as prepared in Example 1, thereby obtaining an impregnated porous polymer sheet, and an excess electrolytic liquid on the surface of the obtained sheet was removed by wiping the surface of the sheet. The impregnated porous polymer sheet was sandwiched between two glass plates, followed by heating at 100 DEG C. As a result of the heating, a sheet deformed into a circular shape was obtained. The gel content of the deformed sheet was 0 %, as measured by the method described above.

[0081] In addition, using the impregnated porous polymer sheet obtained prior to the heating, a sheet battery was prepared in substantially the same manner as described in Example 1. The obtained sheet battery was subjected to a charging operation, and as a result, it was found that a short circuiting occurred, so that it was impossible to charge the sheet battery.

Example 2

[0082] A porous polymer sheet having a thickness of 25 μm and a void ratio of 73 % was prepared in substantially the same manner as in Example 1, except that the thickness of the liquid film was 100 μm . Then, the prepared porous polymer sheet was irradiated with electron beams (irradiation dose: 15 Mrads) to thereby prepare a crosslinked porous polymer sheet.

[0083] The above-prepared crosslinked porous polymer sheet was immersed in substantially the same electrolytic liquid as that prepared in Example 1. When the crosslinked porous polymer sheet was immersed in the electrolytic liquid at room temperature, the sheet was immediately impregnated with the electrolytic liquid, and an impregnated transparent porous polymer sheet was obtained with ease. The electrolytic liquid on the surface of the impregnated porous polymer sheet (that is, an excess electrolytic liquid which did not

impregnate the porous polymer sheet) was removed by wiping the porous polymer sheet. No change in the size of the impregnated porous polymer sheet was observed between the impregnated porous polymer sheet and the non-impregnated porous polymer sheet before the immersion in the electrolytic liquid. For the evaluation of the ionic conductivity of the impregnated porous polymer sheet, the impregnated porous polymer sheet was sandwiched between two stainless steel sheets, to thereby obtain a precursory electrochemical cell in which the impregnated porous polymer sheet is not swelled. The obtained precursory electrochemical cell was subjected to a measurement of an alternating-current impedance, using the above-mentioned two stainless sheets as electrodes. As a result, it was found that the ionic conductivity of the impregnated porous polymer sheet at room temperature was 0.25 mS/cm. The precursory electrochemical cell was heated at 100 DEG C for 1 hour, followed by cooling to room temperature, to thereby obtain an electrochemical cell composed of two electrodes and a hybrid electrolyte sheet (a swollen form of the impregnated porous polymer sheet). The resultant electrochemical cell was subjected to a measurement of an alternating-current impedance in substantially the same manner as described above. As a result, it was found that the ionic conductivity of the hybrid electrolyte sheet at room temperature was 1.1 mS/cm.

[0084] From the above-mentioned impregnated porous polymer sheet was cut out a sample having a size of 15 mm x 15 mm, and then, the sample was sandwiched between two glass plates and heated at 100 DEG C in an oven for 1 hour. The change in the size of the sheet was 1 mm or less in the longitudinal direction of the sheet. The polymer sheet obtained after the heat treatment could be easily handled with forceps. On the other hand, when the crosslinked porous polymer sheet was immersed in the electrolytic liquid at 100 DEG C for 1 hour, the size of the sheet increased from 1.5 cm x 1.5 cm to 2 cm x 2 cm. Thus, the above-mentioned temperature was confirmed to be a temperature at which the crosslinked porous polymer sheet can be swelled with the electrolytic liquid.

Comparative Example 2

[0085] Using substantially the same non-crosslinked porous polymer sheet as prepared in Example 2, a precursory electrochemical cell in which the impregnated porous polymer sheet is not swelled was obtained in substantially the same manner as in Example 2. The obtained precursory electrochemical cell was heated at 100 DEG C for 1 hour, followed by cooling to room temperature, to thereby obtain an electrochemical cell composed of two electrodes and a swollen, impregnated porous polymer sheet. Subsequently, the obtained electrochemical cell was subjected to a measurement of an alternating-current impedance. As a result, it was found that a short circuiting occurred. Furthermore, when the non-crosslinked porous polymer sheet was immersed in the electrolytic liquid at 90 DEG C, the polymer sheet dissolved in 4 minutes.

Example 3 and Comparative Example 3

[0086] From substantially the same LiCoO₂ electrode sheet and needle coke electrode sheet as prepared as in Example 1 were individually cut out a sample having a size of 2 cm x 2 cm. From substantially the same impregnated porous polymer sheet as prepared in Example 2 was cut out a sample having a size of 2.3 cm x 2.3 cm, and the sample of the impregnated porous polymer sheet was sandwiched between the above-prepared electrode sheets so as to obtain a laminate structure, thereby preparing a battery composed of a negative electrode (needle cokes), an impregnated porous polymer sheet, and a positive electrode (LiCoO₂). Subsequently, stainless steel sheets (as electric terminals for taking a current) were brought into contact with the respective current collectors of the positive and negative electrodes of the battery. The battery was then placed in a sealable glass cell having electric terminals for taking a current from the battery (hereinafter frequently referred to simply as "glass cell"), and the electric terminals of the battery were connected to the electric terminals of the cell. The cell was sealed in an argon atmosphere to obtain a sheet battery.

[0087] Two sheet batteries were prepared as described above. One of the sheet batteries was heated at 100 DEG C for 2 hours, followed by cooling to room temperature (Example 3). The other sheet battery was used without being subjected to the heat treatment (Comparative Example 3).

[0088] Both sheet batteries were individually subjected to a measurement of an alternating-current impedance and to charge/discharge cycle testing. As a result of the measurement of an alternating-current impedance, it was found that the internal resistance of the sheet battery of Comparative Example 3 was 80 OMEGA, whereas the internal resistance of the sheet battery of Example 3 was 30 OMEGA. Further, the two batteries

were subjected to charge/discharge cycle testing in substantially the same manner as in Example 1. As a result of the charge/discharge cycle testing, it was found that the discharge/charge efficiency (ratio) at the first cycle of each battery was 80 % or more, and with respect to the cycles after the first cycle, each of the discharge/charge efficiencies (ratio) at both batteries was 99 % or more. These results show that both batteries are capable of being repeatedly charged and discharged and hence operable as a secondary battery. However, the overpotential of the battery of Example 3 was 50 mV, whereas the overpotential of the battery of Comparative Example 3 was 100 mV. Thus, the electric capacity of the sheet battery of Comparative Example 3 was low.

Example 4

[0089] Substantially the sample crosslinked porous polymer sheet as prepared in Example 2 was sandwiched between substantially the same two electrode sheets as prepared in Example 1, to thereby prepare a laminate structure. The prepared laminate structure was immersed in an electrolytic liquid, which is substantially the same as that prepared in Example 1, at room temperature for 1 hour so that the laminate structure was impregnated with the electrolytic liquid, thereby preparing a battery. The electrolytic liquid on the surface of the battery was removed by wiping the battery. Subsequently, stainless steel sheets (as electric terminals for taking a current) were brought into contact with the respective current collectors of the positive and negative electrodes of the battery. The battery was then placed in a glass cell, and the electric terminals of the battery were connected to the electric terminals of the cell. The cell was sealed in an argon atmosphere to obtain a sheet battery. The obtained sheet battery was heated at 100 DEG C for 2 hours, followed by cooling to room temperature.

[0090] The resultant sheet battery was subjected to a measurement of an alternating-current impedance and to charge/discharge cycle testing in substantially the same manner as described in Example 3. As a result of the measurement of an alternating-current impedance, it was found that the internal resistance of the battery was 30 OMEGA . The charging operation was conducted at a constant potential of 4.2 V. After the charging operation, the potential between the electrodes was 4.2 V. The discharging operation was conducted at a constant current, and discontinued when the electric potential was decreased to 2.7 V. As a result of the charge/discharge cycle testing, it was found that the discharge/charge efficiency (ratio) at the first cycle was 80 % or more, and with respect to the cycles after the first cycle, each of the discharge/charge efficiencies (ratio) was 99 % or more. These results show that this battery is capable of being repeatedly charged and discharged and hence operable as a secondary battery. The overpotential of the sheet battery was 30 mV.

Example 5

[0091] A crosslinked porous polymer sheet was prepared in substantially the same manner as in Example 1, except that a vinylidene fluoride homopolymer resin (Kynar 460, manufactured and sold by Elf Atochem North America Inc., USA) was used instead of the hexafluoropropylene/vinylidene fluoride copolymer resin. The thickness of the prepared polymer sheet was 45 μ m and the void ratio was 71 %.

[0092] The above-prepared crosslinked porous polymer sheet was immersed in substantially the same electrolytic liquid as prepared in Example 1. When the crosslinked porous polymer sheet was immersed in the electrolytic liquid at room temperature, the sheet was impregnated with the electrolytic liquid and a transparent impregnated porous sheet was obtained. The change in the size of the impregnated porous polymer sheet was 3 % in the longitudinal direction of the sheet, relative to the size of the non-impregnated porous polymer sheet. The impregnated porous polymer sheet was sandwiched between two glass plates and heated at 120 DEG C in an oven for 2 hours, to thereby prepare a hybrid electrolyte sheet. No change in the size of the impregnated porous polymer sheet was observed between the impregnated porous polymer sheet before the heat treatment and the hybrid electrolyte sheet obtained after the heat treatment. From the prepared hybrid electrolyte sheet was cut out a sample having a predetermined size, and the electrolytic liquid was removed by extraction, followed by drying, to thereby obtain a dried polymer matrix. The degree of shrinkage of the porous polymer sheet was 24 %, as calculated from the size of the dried polymer matrix and the size of the hybrid electrolyte sheet, and the gel content of the polymer matrix was 69 %. On the other hand, when the above-obtained crosslinked porous polymer sheet was immersed in the electrolytic liquid at 120 DEG C for 1 hour, the size of the porous polymer sheet increased by 40 % in the longitudinal direction of the sheet, based on the size of the porous polymer sheet before the immersion in the electrolytic liquid. Thus, the above-mentioned temperature was confirmed to be a temperature at which the porous polymer sheet can be

swelled with the electrolytic liquid. The ionic conductivity of the obtained hybrid electrolyte was 1.1 mS/cm at room temperature.

[0093] From substantially the same LiCoO₂ electrode sheet and needle coke electrode sheet as prepared in Example 1 were individually cut out a sample having a size of 4 cm x 4 cm. From substantially the same impregnated porous polymer sheet as prepared in Example 2 was cut out a sample having a size of 4.5 cm x 4.5 cm, and the sample of the impregnated porous polymer sheet was sandwiched between the above-prepared electrode sheets so as to obtain a laminate structure, thereby preparing a battery composed of a negative electrode (needle cokes), an impregnated porous polymer sheet, and a positive electrode (LiCoO₂). The prepared battery was pressed at 120 DEG C for 1 minute. Stainless steel sheets (as electric terminals for taking a current) were brought into contact with the respective current collectors of the positive and negative electrodes of the resultant heat-pressed battery, and the battery was placed between two opposite PET/Al/PE laminate films (PET: polyethylene terephthalate film, Al: aluminum sheet, PE: polyethylene film) so that the current collectors project from the resultant structure. The laminate structure of the resultant structure was made secure by means of a laminator, to thereby obtain a sheet battery.

[0094] The sheet battery was subjected to charge/discharge cycle testing in substantially the same manner as described in Example 1. As a result of the charge/discharge cycle testing, it was found that the discharge/charge efficiency (ratio) at the first cycle was 80 % or more, and with respect to the cycles after the first cycle, each of the discharge/charge efficiencies (ratio) was 99 % or more. These results show that this battery is capable of being repeatedly charged and discharged and hence operable as a secondary battery.

[0095] After repeating the charge/discharge testing ten cycles, both of the two opposite PET/Al/PE laminate films were removed from the sheet battery, thereby isolating the battery. An attempt was made to remove the electrode sheets from the isolated battery; however, only the current collectors (metal sheets) came off the battery, thus demonstrating that the electrode sheets are securely attached to both sides of the electrolyte sheet.

Example 6

[0096] A crosslinked porous polymer sheet was prepared in substantially the same manner as in Example 1, except that a vinylidene fluoride homopolymer resin (Trade name: Kynar 740, manufactured and sold by Elf Atochem North America Inc., U.S.A.) was used instead of the hexafluoropropylene/vinylidene fluoride copolymer resin. The prepared crosslinked porous polymer sheet had a thickness of 60 μ m and a void ratio of 77 %. The crosslinked porous polymer sheet was immersed in an electrolytic liquid in substantially the same manner as in Example 1, to thereby obtain an impregnated transparent porous polymer sheet. The change in the size of the impregnated crosslinked porous polymer sheet was 3 % in the longitudinal direction of the sheet. The impregnated porous polymer sheet was sandwiched between two glass plates and heated at 120 DEG C in an oven for 2 hours, to thereby obtain a hybrid electrolyte sheet. No change in the size of the impregnated porous polymer sheet was observed between the impregnated porous polymer sheet before the heat treatment and the hybrid electrolyte sheet obtained after the heat treatment. From the electrolyte sheet was cut out a sample having a predetermined size, and the electrolytic liquid was removed by extraction, followed by drying, to thereby obtain a dried polymer matrix. The degree of shrinkage of the porous polymer sheet was 24 %, as calculated from the size of the dried polymer matrix and the size of the hybrid electrolyte sheet, and the gel content of the polymer matrix was 40 %. On the other hand, when the above-obtained crosslinked porous polymer sheet was immersed in the electrolytic liquid at 120 DEG C for 1 hour, the size of the crosslinked porous polymer sheet increased by 38 % in the longitudinal direction of the sheet, based on the size of the porous polymer sheet before the immersion in the electrolytic liquid. Thus, the above-mentioned temperature was confirmed to be a temperature at which the porous polymer sheet can be swelled with the electrolytic liquid. The ionic conductivity of the hybrid electrolyte sheet at room temperature was 1.4 mS/cm.

[0097] Using the hybrid electrolyte sheet obtained above, a sheet battery was prepared in substantially the same manner as described in Example 5, and the prepared sheet battery was subjected to charge/discharge cycle testing. As a result of the charge/discharge cycle testing, it was found that the discharge/charge efficiency (ratio) at the first cycle was 80 % or more, and with respect to the cycles after the first cycle, each of the discharge/charge efficiencies (ratio) was 99 % or more. These results show that this battery is capable of being repeatedly charged and discharged and hence operable as a secondary battery.

[0098] After repeating the charge/discharge testing ten cycles, both of the two opposite PET/Al/PE laminate films were removed from the sheet battery, thereby isolating the battery. An attempt was made to remove the electrode sheets from the isolated battery; however, only the current collectors (metal sheets) came off the battery, thus demonstrating that the electrode sheets are securely attached to both sides of the electrolyte sheet.

Comparative Example 4

[0099] Substantially the same crosslinked porous polymer sheet as used in Example 5, that is, the crosslinked porous polymer sheet used for confirming the conditions at which the porous polymer sheet can be swelled with the electrolytic liquid, was used for preparing a hybrid electrolyte sheet. The crosslinked porous polymer sheet was immersed in substantially the same electrolytic liquid as used in Example 5 at 120 DEG C for 1 hour, to thereby obtain a hybrid electrolyte sheet. From the obtained hybrid electrolyte sheet was cut out a sample having a predetermined size, and the electrolytic liquid was removed by extraction, followed by drying, to thereby obtain a dried polymer matrix. The degree of shrinkage of the porous polymer sheet was 36 %, as calculated from the size of the dried polymer matrix and the size of the hybrid electrolyte sheet, and the gel content of the polymer matrix was 86 %. The ionic conductivity of the hybrid electrolyte sheet at room temperature was 1.8 mS/cm.

[0100] Using the hybrid electrolyte sheet obtained above, a sheet battery was prepared in substantially the same manner as in Example 5, and the prepared sheet battery was subjected to charge/discharge cycle testing ten cycles. As a result of the charge/discharge cycle testing, it was found that the charge/discharge efficiencies were unstable. After repeating the charge/discharge testing ten cycles, both of the two opposite PET/Al/PE laminate films were removed from the sheet battery, thereby isolating the battery. Then, the electrode sheets were removed from the isolated battery. Though some of the LiCO₂ particles or the needle coke particles remain on the surface of the electrolyte sheet, almost all of the electrode sheets were removed from the electrolyte sheet, thus demonstrating that the electrode sheets are inadequately attached to both sides of the electrolyte sheet.

Example 7

[0101] A conventional porous membrane filter made from polyvinylidene fluoride resin (diameter: 0.22 μ m, thickness: 125 μ m, and a void ratio: 75 %) (Durapore GVHP, manufactured and sold by MILLIPORE Japan, Japan) was irradiated with electron beams (irradiation dose: 30 Mrad) to thereby prepare a crosslinked porous polymer sheet. The resultant crosslinked porous polymer sheet was immersed in an electrolytic liquid in substantially the same manner as in Example 1. When the crosslinked porous polymer sheet was immersed in the electrolytic liquid, the sheet was immediately impregnated with the electrolytic liquid and an impregnated transparent porous polymer sheet was obtained. No change in the size of the impregnated porous polymer sheet was observed between the impregnated polymer sheet and the porous polymer sheet before the immersion in the electrolytic liquid. The impregnated porous polymer sheet was sandwiched between two glass plates and heated at 120 DEG C in an oven for 2 hours, to thereby obtain a hybrid electrolyte sheet. No change in the size of the impregnated porous polymer sheet was observed between the impregnated porous polymer sheet before the heat treatment and the hybrid electrolyte sheet obtained after the heat treatment. From the obtained hybrid electrolyte sheet was cut out a sample having a predetermined size, and the electrolytic liquid was removed by extraction, followed by drying, to thereby obtain a dried polymer matrix. The degree of shrinkage of the porous polymer sheet was 20 %, as calculated from the size of the dried polymer matrix and the size of the hybrid electrolyte sheet, and the gel content of the polymer matrix was 72 %. On the other hand, when the above-obtained crosslinked porous polymer sheet was immersed in the electrolytic liquid at 120 DEG C for 1 hour, the size of the crosslinked porous polymer sheet increased by 40 % in the longitudinal direction of the sheet. Thus, the above-mentioned temperature was confirmed to be a temperature at which the crosslinked porous polymer sheet can be swelled with the electrolytic liquid. The ionic conductivity of the obtained hybrid electrolyte sheet at room temperature was 1.2 mS/cm.

[0102] Using the above-obtained hybrid electrolyte sheet, a sheet battery was prepared in substantially the same manner as in Example 5, and the obtained sheet battery was subjected to charge/discharge cycle testing. As a result of the charge/discharge cycle testing, it was found that the discharge/charge efficiency (ratio) at the first cycle was 80 % or more, and with respect to the cycles after the first cycle, each of the discharge/charge efficiencies (ratio) was 99 % or more. These results show that this battery is capable of

being repeatedly charged and discharged and hence operable as a secondary battery.

[0103] After repeating the charge/discharge testing ten cycles, both of the two opposite PET/Al/PE laminate films were removed from the sheet battery, thereby isolating the battery. An attempt was made to remove the electrode sheets from the isolated battery; however, only the current collectors (metal sheets) came off the battery, thus demonstrating that the electrode sheets are securely attached to both sides of the electrolyte sheet.

Comparative Example 5

[0104] A mixture consisting of 2 parts by weight of a hexafluoropropylene/vinylidene fluoride copolymer resin (Trade name: KynarFlex 2801, manufactured and sold by Elf Atochem North America Inc., U.S.A.), 2 parts by weight of dibutyl phthalate and 10 parts by weight of acetone was prepared and heated at 50 DEG C, to thereby melt the copolymer. The resultant mixture was cast on a plate at a thickness of 0.5 mm and dried in air, thereby obtaining a liquid film having a thickness of 90 μ m. The obtained liquid film was subjected to extraction with ether, to thereby remove dibutyl phthalate contained in the film. The resultant film was dried to obtain a non-porous polymer sheet. The obtained non-porous polymer sheet was irradiated with electron beams (irradiation dose: 15 Mrad) to thereby obtain a crosslinked non-porous polymer sheet. The crosslinked non-porous polymer sheet was immersed in substantially the same electrolytic liquid as prepared in Example 1 at 50 DEG C, thereby obtaining an electrolytic liquid-impregnated, swollen non-porous polymer sheet as hybrid electrolyte sheet. The change in the size of the swollen hybrid electrolyte sheet was 25 % in the longitudinal direction of the sheet. The degree of shrinkage of the hybrid electrolyte sheet was 25 %, as calculated from the size of the dried polymer matrix and the size of the hybrid electrolyte sheet, and the gel content of the polymer matrix was 55 %. The ionic conductivity of the hybrid electrolyte sheet at room temperature was 0.3 mS/cm.

[0105] Using the hybrid electrolyte sheet obtained above, a sheet battery was prepared in substantially the same manner as described in Example 5, except that the hybrid electrolyte sheet and the electrode sheets were pressed against each other at 100 DEG C. The prepared sheet battery was subjected to charge/discharge cycle testing ten cycles. As a result of the charge/discharge cycle testing, it was found that all of the discharge/charge efficiencies were low, and the discharge capacity at the tenth cycle was only 40 % of that at the first cycle. These results show that the properties of this battery are insufficient to operate as a secondary battery.

Example 8

[0106] Substantially the same crosslinked porous polymer sheet as prepared in Example 1 was placed in a petri dish preheated to 100 DEG C. Substantially the same electrolytic liquid as prepared in Example 1 was heated to 100 DEG C, and the heated electrolytic liquid was dropwise applied to the entire surface of the crosslinked porous polymer sheet in the petri dish until the white color of the crosslinked porous polymer sheet disappeared and the polymer sheet became transparent, thus impregnating the crosslinked porous polymer sheet with the electrolytic liquid. The impregnated porous polymer sheet was cooled to room temperature, thereby obtaining an electrolytic liquid-impregnated, swollen porous polymer sheet as a hybrid electrolyte sheet. The size of the hybrid electrolyte sheet increased by 30 % in the longitudinal direction thereof, relative to the size of the porous polymer sheet as measured before the impregnating with the electrolytic liquid. This confirmed that the porous polymer sheet was swelled with the electrolytic liquid. From the obtained hybrid electrolyte sheet was cut out a sample having a predetermined size, and the electrolytic liquid was removed by extraction, followed by drying, to thereby obtain a dried polymer matrix. The degree of shrinkage of the porous polymer sheet was 36 %, as calculated from the size of the dried polymer matrix and the size of the hybrid electrolyte sheet, and the gel content of the polymer matrix was 70 %. The ionic conductivity of the hybrid electrolyte sheet was 1.6 mS/cm.

[0107] Using the hybrid electrolyte sheet obtained above, a sheet battery was prepared in substantially the same manner as described in Example 5, except that the hybrid polymeric electrolyte sheet and the electrode sheets were pressed against each other at 100 DEG C. The prepared sheet battery was subjected to charge/discharge cycle testing. As a result of the charge/discharge cycle testing, it was found that the discharge/charge efficiency (ratio) at the first cycle was 80 %, and with respect to the cycles after the first cycle, each of the discharge/charge efficiencies (ratio) was 99 % or more. These results show that this battery

is capable of being repeatedly charged and discharged and hence operable as a secondary battery.

[0108] After repeating the charge/discharge testing ten cycles, both of the two opposite PET/Al/PE laminate films were removed from the sheet battery, thereby isolating the battery. An attempt was made to remove the electrode sheets from the isolated battery; however, only the current collectors (metal sheets) came off the battery, thus demonstrating that the electrode sheets are securely attached to the electrolyte sheet.

Example 9

[0109] From substantially the same LiCoO₂ electrode sheet and needle coke electrode sheet as prepared in Example 1 were individually cut out a sample having a size of 4 cm x 4 cm. From substantially the same crosslinked porous polymer sheet as prepared in Example 1 was cut out a sample having a size of 4.5 cm x 4.5 cm, and the sample of the crosslinked porous polymer sheet was sandwiched between the above-prepared electrode sheets so as to obtain a laminate structure composed of a negative electrode (needle cokes), a porous polymer sheet, and a positive electrode (LiCoO₂). The obtained laminate structure was sandwiched between two glass plates and held by means of a clip. The sandwiched structure was heated to 100 DEG C, and then, the heated, sandwiched structure was held with its one side edge directed upward. Substantially the same electrolytic liquid as prepared in Example 1 was heated to 100 DEG C, and the heated electrolytic liquid was dropwise applied to the side edge of the laminate structure held between the glass plates until an excess electrolytic liquid began to flow down from the structure, to thereby impregnate the crosslinked porous polymer sheet with the electrolytic liquid. Subsequently, the resultant laminate structure was cooled to room temperature, thereby obtaining a battery. The glass plates were removed from the obtained battery, and stainless sheets (as electric terminals for taking a current) were brought into contact with the respective current collectors of the positive and negative electrodes of the battery. The battery was placed between two opposite PET/Al/PE laminate films so that the ends of the current collectors project from the resultant structure. The laminate structure of the resultant structure was made secure by means of a laminator, to thereby obtain a sheet battery.

[0110] The obtained sheet battery was subjected to charge/discharge cycle testing in substantially the same manner as in Example 1. As a result of the charge/discharge cycle testing, the discharge/charge efficiency (ratio) at the first cycle was 80 % or more. With respect to the cycles after the first cycle, each of the discharge/charge efficiencies (ratio) was 99 % or more. These results show that this battery is capable of being repeatedly charged and discharged and hence operable as a secondary battery.

[0111] After repeating the charge/discharge testing ten cycles, both of the two opposite PET/Al/PE laminate films were removed from the sheet battery, thereby isolating the battery. An attempt was made to remove the electrode sheets from the isolated battery; however, only the current collectors (metal sheets) came off the battery, thus demonstrating that the electrode sheets are securely attached to both sides of the electrolyte sheet. In this situation, after removing the current collectors from the battery, the electrolyte layer of the battery, together with the electrode layers, was washed with ethanol, followed by an extraction of the electrolytic liquid. Then, a major portion of each of the electrode layers on both surfaces of the electrolyte layer was scraped off, thereby obtaining a polymer sheet. Further, the obtained polymer sheet was dried to thereby obtain a sheet of dried polymer matrix. The degree of shrinkage of the porous polymer sheet after drying was 14 % and the gel content of the dried polymer matrix was 65 %.

Example 10 and 11

[0112] A solution consisting of 17 parts by weight of polyacrylonitrile and 83 parts by weight of dimethyl sulfoxide was prepared, and the prepared solution was cast on a glass plate at room temperature, thereby preparing a liquid film having a thickness of 100 μ m. Immediately, the obtained liquid film was immersed in water at room temperature to thereby solidify the film, and then, the film was washed with water and alcohol, followed by drying, thereby obtaining a porous polymer sheet having a thickness of 95 μ m, and a void ratio of 78 % (Example 10).

[0113] The above-prepared solution was cast on a glass plate at 60 DEG C, to thereby obtain a liquid film having a thickness of 100 μ m. Immediately, the obtained liquid film was immersed in water at 70 DEG C to thereby solidify the film, and then, the film was washed with water and alcohol, followed by drying, thereby obtaining a porous polymer sheet having a thickness of 76 μ m, and a void ratio of 81 % (Example 11).

[0114] The above-obtained two different porous polymer sheets were irradiated with electron beams (irradiation dose: 30 Mrads) to thereby obtain crosslinked porous polymer sheets. Each of the crosslinked porous polymer sheets was immersed in a mixed solvent of ethylene carbonate (EC) and propylene carbonate (PC) (EC/PC weight ratio = 1/1); however, none of the porous polymer sheets dissolved in the mixed solvent, thus confirming that the porous polymers are crosslinked.

[0115] An electrolytic liquid was obtained by dissolving LiBF_4 into a mixed solvent of ethylene carbonate (EC) and propylene carbonate (PC) (EC/PC weight ratio = 1/1, and LiBF_4 concentration: 1 mol/liter), and the crosslinked porous polymer sheets were individually immersed in the above-obtained electrolytic liquid at room temperature for 30 minutes, to thereby obtain impregnated transparent porous polymer sheets impregnated with the electrolytic liquid. Each of the obtained impregnated porous polymer sheets of Example 10 and 11 had a thickness of 103 μm and 85 μm , respectively. With respect to the size of each impregnated porous polymer sheet, no change was observed between the impregnated porous polymer sheet and the non-impregnated porous polymer sheet. An excess electrolytic liquid on the surface of each impregnated porous polymer sheet was removed by wiping the porous polymer sheet. For the evaluation of the ionic conductivity of each of the impregnated porous polymer sheets, the impregnated porous polymer sheets were individually sandwiched between two stainless steel sheets (as electrodes), to thereby obtain precursory electrochemical cells in which the impregnated porous polymer sheets are not swelled. Each of the obtained precursory electrochemical cells was subjected to a measurement of an alternating current impedance. As a result, it was found that the impregnated porous polymer sheets of Examples 10 and 11 had an ionic conductivity at room temperature of 0.3 mS/cm and 0.4 mS/cm, respectively. The precursory electrochemical cells were individually heated at 100 DEG C for 1 hour and cooled to room temperature, to thereby obtain electrochemical cells each composed of two electrodes and a hybrid electrolyte sheet (a swollen form of the impregnated porous polymer sheet). Each of the resultant electrochemical cells was subjected to a measurement of an alternating current impedance in substantially the same manner as described above. As a result, it was found that the hybrid electrolyte sheets of Examples 10 and 11 had an ionic conductivity at room temperature of 1.2 mS/cm and 1.4 mS/cm, respectively. With respect to each of the electrochemical cells of Examples 10 and 11, no change in the size of the impregnated porous polymer sheets was observed between the impregnated porous polymer sheets before the heat treatment and the hybrid electrolyte sheets obtained after the heat treatment.

[0116] On the other hand, when the crosslinked porous polymer sheets were individually immersed in the above-prepared electrolytic liquid at 100 DEG C for 1 hour, transparent, electrolytic liquid-impregnated, swollen porous polymer sheets of Example 10 and 11 were obtained. The surface area of the sheet obtained in Example 10 increased by 350 % and the surface area of the sheet obtained in Example 11 increased by 290 %, based on the surface area of the crosslinked porous polymer sheet before being swelled with the electrolytic liquid.

Example 12

[0117] A solution consisting of 17 parts by weight of a hexafluoropropylene/vinylidene fluoride copolymer resin (trade name: Kynar Flex 2801, manufactured and sold by Elf Atochem North America Inc., U.S.A.), 15 parts by weight of polyvinylpyrrolidone (trade name: K-30, manufactured and sold by Tokyo Kasei Ltd., Japan) and 68 parts by weight of N-methylpyrrolidone was prepared, and the prepared solution was cast on a glass plate at 50 DEG C, to thereby obtain a liquid film having a thickness of 200 μm . Immediately, the obtained liquid film was immersed in a mixed solvent of N-methylpyrrolidone and water (weight ratio: 75/25) at room temperature, to thereby solidify the film, and then, the film was washed with water and alcohol, followed by drying, thereby obtaining a porous polymer sheet having a thickness of 61 μm and a void ratio of 64 %. Further, the obtained porous polymer sheet was irradiated with electron beams (irradiation dose: 10 Mrads), to thereby obtain a crosslinked porous polymer sheet.

[0118] The above-obtained crosslinked porous polymer sheet was immersed in substantially the same electrolytic liquid as prepared in Example 1. When the crosslinked porous polymer sheet was immersed in the electrolytic liquid at room temperature, the sheet was immediately impregnated with the electrolytic liquid, thereby obtaining an impregnated transparent porous polymer sheet. The obtained impregnated transparent porous polymer sheet was sandwiched between two glass plates, and heated at 100 DEG C in an oven for 2 hours, to thereby obtain a hybrid electrolyte sheet. No change in the size of the impregnated porous polymer sheet was observed between the impregnated porous polymer sheet before the heat treatment and the hybrid electrolyte sheet obtained after the heat treatment. From the electrolyte sheet was cut out a sample having a

predetermined size, and the electrolytic liquid was removed by extraction, followed by drying, to thereby obtain a dried polymer matrix. The degree of shrinkage of the porous polymer sheet was 42 %, as calculated from the size of the dried polymer matrix and the size of the hybrid electrolyte sheet, and the gel content of the polymer matrix was 58 %. The ionic conductivity of the hybrid electrolyte sheet at room temperature was 1.3 mS/cm.

[0119] Using the hybrid electrolyte sheet obtained above, a sheet battery was prepared in substantially the same manner as described in Example 5, except that the hybrid electrolyte sheet and the electrode sheets were pressed against each other at 100 DEG C. The prepared sheet battery was subjected to charge/discharge testing. As a result of the charge/discharge cycle testing, it was found that the discharge/charge efficiency (ratio) at the first cycle was 80 % or more, and with respect to the cycles after the first cycle, each of the discharge/charge efficiencies (ratio) was 99 % or more. These results show that this battery is capable of being repeatedly charged and discharged and hence operable as a secondary battery.

[0120] After repeating the charge/discharge testing ten cycles, both of the two opposite PET/Al/PE laminate films were removed from the sheet battery, thereby isolating the battery. An attempt was made to remove the electrode sheets from the isolated battery; however, only the current collectors (metal sheets) came off the battery, thus demonstrating that the electrode sheets are securely attached to both sides of the electrolyte sheet.

Example 13

[0121] Substantially the same crosslinked porous polymer sheet and an electrolytic liquid as prepared in Example 10 were used to impregnate the crosslinked porous polymer sheet with the electrolytic liquid in substantially the same manner as in Example 10, to thereby obtain an impregnated porous polymer sheet. The obtained impregnated porous polymer sheet was sandwiched between two glass plates and heated at 100 DEG C in an oven for 1 hour, to thereby obtain a hybrid electrolyte sheet. No change in the size of the impregnated porous polymer sheet was observed between the impregnated porous polymer sheet before the heat treatment and the hybrid electrolyte sheet obtained after the heat treatment. From the obtained hybrid electrolyte sheet was cut out a sample having a predetermined size, and the electrolytic liquid was removed by extraction, followed by drying, to thereby obtain a dried polymer matrix. The degree of shrinkage of the porous polymer sheet was 50 %, as calculated from the size of the dried polymer matrix and the size of the hybrid electrolyte sheet, and the gel content of the polymer matrix was 37 %. The ionic conductivity of the hybrid electrolyte sheet at room temperature was 1.4 mS/cm.

*[0122] Using the hybrid electrolyte sheet obtained above, a sheet battery was prepared in substantially the same manner as described in Example 5. The prepared sheet battery was subjected to charge/discharge cycle testing. As a result of the charge/discharge cycle testing, it was found that the discharge/charge efficiency (ratio) at the first cycle was 80 % or more, and with respect to the cycles after the first cycle, each of the discharge/charge efficiencies (ratio) was 99 % or more. These results show that this battery is capable of being repeatedly charged and discharged and hence operable as a secondary battery.

[0123] After repeating the charge/discharge testing ten cycles, both of the two opposite PET/Al/PE laminate films were removed from the sheet battery, thereby isolating the battery. An attempt was made to remove the electrode sheets from the isolated battery, but only the current collectors (metal sheets) came off the battery, thus demonstrating that the electrode sheets are securely attached to both sides of the electrolyte sheet.

INDUSTRIAL APPLICABILITY

[0124] The hybrid electrolyte of the present invention has a high ionic conductivity, an excellent stability under high temperature conditions and an excellent adherability to an electrode, so that the hybrid electrolyte of the present invention can be advantageously used as an electrolyte for various electrochemical devices, such as primary and secondary batteries (e.g., a lithium battery), a photoelectrochemical device and an electrochemical sensor. Further, by the method of the present invention, the hybrid electrolyte having the above-mentioned excellent properties and an electrochemical device comprising such a hybrid electrolyte can be surely and effectively produced.



PCT

特許協力条約に基づいて公開された国際出願

<p>(51) 国際特許分類6 H01B 1/12</p>	<p>A1</p>	<p>(11) 国際公開番号 WO97/48106</p> <p>(43) 国際公開日 1997年12月18日(18.12.97)</p>						
<p>(21) 国際出願番号 PCT/JP97/02056</p> <p>(22) 国際出願日 1997年6月13日(13.06.97)</p> <p>(30) 優先権データ</p> <table border="0"> <tr> <td>特願平8/152134</td> <td>1996年6月13日(13.06.96)</td> <td>JP</td> </tr> <tr> <td>特願平9/100397</td> <td>1997年4月17日(17.04.97)</td> <td>JP</td> </tr> </table> <p>(71) 出願人 (米国を除くすべての指定国について) 旭化成工業株式会社 (ASAHI KASEI KOGYO KABUSHIKI KAISHA)[JP/JP] 〒530 大阪府大阪市北区堂島浜1丁目2番6号 Osaka, (JP)</p> <p>(72) 発明者 ; および</p> <p>(75) 発明者 / 出願人 (米国についてののみ)</p> <p>星 信人(HOSHI, Nobuto)[JP/JP] 〒710 岡山県倉敷市福井306-8 サンシャインB205 Okayama, (JP)</p> <p>黒木正勝(KUROKI, Masakatsu)[JP/JP] 〒416 静岡県富士市川成島100 旭化成富士第5寮110 Shizuoka, (JP)</p> <p>南方 尚(MINAKATA, Takashi)[JP/JP] 〒421-33 静岡県庵原郡富士川町中野台1-15-5 Shizuoka, (JP)</p>		特願平8/152134	1996年6月13日(13.06.96)	JP	特願平9/100397	1997年4月17日(17.04.97)	JP	<p>(74) 代理人 弁理士 片桐光治(KATAGIRI, Mitsuji) 〒107 東京都港区赤坂4丁目3番1号 共同ビル赤坂312号 Tokyo, (JP)</p> <p>(81) 指定国 CA, CN, JP, KR, MX, US, 欧州特許 (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>添付公開書類 国際調査報告書</p>
特願平8/152134	1996年6月13日(13.06.96)	JP						
特願平9/100397	1997年4月17日(17.04.97)	JP						
<p>(54)Title: HYBRID ELECTROLYTE, METHOD FOR MANUFACTURING THE SAME, AND METHOD FOR MANUFACTURING ELECTROCHEMICAL ELEMENT USING THE SAME</p> <p>(54)発明の名称 ハイブリッド電解質、該電解質の製造方法、および該電解質を用いた電気化学素子の製造方法</p> <p>(57) Abstract</p> <p>A hybrid electrolyte which is prepared by impregnating a molded high polymer porous body composed of a high polymer base material containing a cross-linked high polymer segment and a plurality of bubbles dispersed in the base material with an electrolytic solution until the porous body swells, with the high polymer base material having 20-75 gel %, a method for manufacturing the electrolyte, and a method for manufacturing an electrochemical element using the electrolyte. The hybrid electrolyte has high ionic conductivity and excellent high-temperature stability and exhibits a high adhesive property when the electrolyte is stuck to an electrode. In addition, when the method for manufacturing hybrid electrolyte is used, the hybrid electrolyte having the above-mentioned excellent properties and an electrochemical element using the hybrid electrolyte can be manufactured surely and efficiently.</p>								

(57) 要約

架橋された高分子セグメントを含む高分子母材及び該母材中に分散している複数の気泡からなる高分子多孔質成形体が、電解液で含浸・膨潤されてなり、該高分子母材が20～75%のゲル分率を有することを特徴とするハイブリッド電解質、該電解質の製造方法、および該電解質を用いた電気化学素子の製造方法が開示される。本発明のハイブリッド電解質は、イオン伝導度が高く、高温安定性に優れ、電極と接着させる際の接着性に優れている。また、本発明の製造方法を用いることにより、上記のような優れた特徴を有する本発明のハイブリッド電解質および該電解質を用いた電気化学素子を確実に効率よく製造することができる。

参考情報

PCTに基づいて公開される国際出願のパンフレット第一頁に記載されたPCT加盟国を同定するために使用されるコード

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明 細 書

ハイブリッド電解質、該電解質の製造方法、および該電解質を用いた電気化学素子の製造方法

技術分野

本発明は新規なハイブリッド電解質に関する。さらに詳しくは、本発明は架橋された高分子セグメントを含む高分子母材及び該母材中に分散している複数の気泡からなる高分子多孔質成形体が、電解液で含浸・膨潤されてなり、該高分子母材が特定のゲル分率を有することを特徴とするハイブリッド電解質、該電解質の製造方法、および該電解質を用いた電気化学素子の製造方法に関する。

本発明のハイブリッド電解質は、イオン伝導度が高く、高温安定性に優れ、また電極と接着させる際の接着性に優れているので、リチウム電池を初めとする一次電池および二次電池、光電気化学デバイス、電気化学センサーなどの電気化学素子用の電解質として有用である。また、本発明の方法を用いることにより、上記のような優れた特徴を有する本発明のハイブリッド電解質および該電解質を用いた電気化学素子を確実且つ効率よく製造することができる。

従来技術

最近、携帯電話やパソコン等の小型化、軽量化のために高エネルギー密度の電池が要求され、これに対応する電池としてリチウムイオン電池が開発されている。この種の電池は正極および負極の電極間に、電解液に膨潤することのない、多孔質のセパレーターが配置された構造を有しているが、セパレーターに含浸させた電解液の漏出を防ぐため、電池構造体全体を重厚な金属容器でパッケージしたものが製品化されている。

一方、多孔質セパレーターの代わりに固体電解質を用いてセパレーターの役割も同時に果たさせるように構成した、いわゆる固体電池は、液漏れがないため電池の信頼性、安全性が向上するとともに、薄膜化や積層体形成やパッケージの簡略化、軽量化が期待されている。特にイオン伝導性高分子を用いた高分子固体電解質は、加工柔軟性を有するため電極との積層構造体の形成が容易にできるのみならず、イオン吸蔵放出による電極の体積変化に応じて固体電解質の電極との界面が適切に変形するので、電極からの剥離を起こさず、電極との界面が保持されるなど好ましい性質を有すると期待されている。

このような高分子固体電解質の試みとしては、W r i g h tによりポリエチレンオキサイドのアルカリ金属塩複合体が、
B r i t i s h P o l y m e r J o u r n a l , 7 巻,

p 3 1 9 (1 9 7 5 年) に報告されて以来、ポリエチレンオキサイド、ポリプロピレンオキサイドなどのポリエーテル系材料をはじめ、ポリホスファゼン、ポリシロキサンなどを骨格とした高分子固体電解質材料が活発に研究されている。このような高分子固体電解質は、通常は高分子固体中に電解質が均一に溶け込んだとみなされる、いわゆる固溶体の形態をとり、ドライ系高分子固体電解質として知られているが、そのイオン伝導度は電解液に比較して著しく低く、これを用いて構成した電池は充放電電流密度が限定され、電池抵抗が高いなどの問題を有していた。

そのため、より電解液に近い状態を形成させることでイオン伝導度を向上させようとする試みが種々提案されている。例えば、電解質の解離度を向上したり、高分子の分子運動を促進してイオン伝導度を向上させる目的で、電解質を溶解して電解液としうる溶媒である電解質溶媒等を可塑剤として母体高分子に添加し、全体をゲル状としたゲル状固体電解質が知られている（日本国特開昭 5 7 - 1 4 3 3 5 6 号公報等）。このようなゲル状固体電解質の例としては、米国特許第 5 2 9 6 3 1 8 号明細書にはフッ化ビニリデンポリマーに電解液を添加してゲル状とした固体電解質が示されている。さらに米国特許第 5 4 2 9 8 9 1 号明細書には、架橋されたフッ化ビニリデンポリマーに電解液を加えて該架橋ポリマーを膨潤させてゲル状とした固体電解質が示されている。このような

いわゆるハイブリッド電解質を用いて電池を製造する場合、該膨潤架橋ポリマーからなるハイブリッド電解質を製造し、その後に電池を組み立てるという方法が一般的である。このようなハイブリッド電解質の母体高分子としては架橋ポリマーを用いることができるが、一方、未架橋のポリマーと電解質と可塑剤とを低沸点溶媒に溶かした溶液を電極上に塗布し、該低沸点溶媒のみを揮発除去することでハイブリッド電解質層を形成する電池の製造方法も知られている（米国特許第5296318号明細書）。これらの材料は電気化学的に安定な上、従来のドライ系固体電解質をはるかにしのぐイオン伝導度を有していたが、それでも電解液に比べれば十分なものではなかった。このような電解質は空孔をもたないため電池にしたときの容量は高いものではなかった。

さらにイオン伝導度の高いハイブリッド電解質として、ポリマーと電解液からなるゲル相の中に電解液からなる液相部分が分散してなる材料が提案されている。例えば日本国特開平8-250127号公報にはポリフッ化ビニリデン多孔膜を固体電解質の母体として用いることが記載されている。ここでは多孔膜に高温で電解液を含浸させる方法が示されており、本発明におけるハイブリッド電解質と同様の、電解液で含浸・膨潤されてなるハイブリッド電解質を与えるものである。また、日本国特開平6-150939号公報には、架橋処理された極性単位含有ポリマーからなる多孔質体を固体電

解質の母体としてハイブリッド電解質を得る方法が記載されている。しかしながら、これらの特開公報に記載された方法では電解液を保持させるため、多孔膜を構成するポリマーが電解液に溶解する条件下、架橋された多孔膜を大過剰の電解液中に浸漬させる方法がとられており、得られたハイブリッド電解質においては、電極との接着性を付与すべき未架橋成分が電解液中に溶出してしまうため、最終の電解質は電極との接着強度が極めて低いものであった。

また、日本国特開平 8-195220 号公報には、未架橋のポリアクリロニトリルを電解液に分散させた分散液をステンレスからなる基板上に塗布した後、塗布された分散液を該基板上で加熱することにより、該基板上に存在する該分散液中のポリアクリロニトリルを電解液に溶解させて均一な溶液とし、次に該溶液を該基板上で冷却することにより形成された、未架橋のポリアクリロニトリルからなる母体高分子に電解液が保持されたハイブリッド電解質層に、電解質溶液中でステンレス細針で穴をあけ、多孔質にする方法が記載されているが、記載された方法では電解液に溶解させるために未架橋のポリアクリロニトリルを用いる必要があり、またこの方法で得られるハイブリッド電解質の母体高分子であるポリアクリロニトリルを架橋構造とすることは困難である。そのため、この方法で得られるハイブリッド電解質は、高温にさらされると溶解や溶融により変形してしまい、穴がつぶれたり

さらには短絡のおそれがあるという欠点があった。

また、上記した種々のハイブリッド電解質は、そのものが既に膨潤ポリマーからなっているために強度が著しく低く、電池を組み立てる際に、このハイブリッド電解質を積層するための取扱いは容易でなかった。特に高いエネルギー密度を得るための薄膜化は著しく困難なものであった。また、電極上にポリマーと電解質の溶液を塗布する方法では取扱いは容易ながら、THFのような可燃性の低沸点溶媒を使用するために安全上好ましいものではなかった。

一方、液体状イオン伝導体を多孔質膜の空孔内に充填し、毛管作用を利用して保持することで電解質の漏出を防ぐ試みも提案されており、例えば $0.1\mu\text{m}$ 以下の貫通孔径を有する、ポリオレフィンのような高強度の材料の微多孔質膜にイオン移動媒体を充填してなる電解質薄膜が作製されている

(日本国特開平1-158051号公報)。この場合は、強度は大きいものの、多数の孔が複雑に交錯して迷路状になった電解液相をイオンが通るためにイオン伝導度が大きく低下する欠点を有していた。

発明の概要

本発明者らは、上記の従来技術における困難な問題点がなく、高いイオン伝導度を有し、高温安定性に優れ、且つ電極との接着性に優れたハイブリッド電解質、および該電解質な

らびにこれを用いた電池などの電気化学素子を確實且つ効率よく製造する方法を開発すべく鋭意研究を行った。その結果意外にも、架橋された高分子セグメントを含み且つ20～75%のゲル分率を有する高分子母材及び該母材中に分散した複数の気泡からなる高分子多孔質成形体が、電解質の水系または非水系溶媒溶液および液状電解質からなる群より選ばれる電解液で含浸・膨潤されてなるハイブリッド電解質が、高いイオン伝導度を有し、高温安定性に優れ、且つ電極との接着性に優れていることを見出した。

また、上記の高分子多孔質成形体に、上記の電解液によって該高分子多孔質成形体が実質的に膨潤され得ない温度および圧力で、該電解液を含浸させて含浸高分子多孔質成形体を得、該含浸高分子多孔質成形体を該高分子多孔質成形体が該電解液で膨潤され得る温度および圧力下に保持することの特徴とする方法により、上記のハイブリッド電解質を確實且つ効率よく製造することができることを見出した。

さらに、上記の高分子多孔質成形体に、上記の電解液によって該高分子多孔質成形体が実質的に膨潤され得ない温度および圧力で、該電解液を含浸させて含浸高分子多孔質成形体を得、該含浸高分子多孔質成形体を電極と積層して積層体を得、該積層体を該高分子多孔質成形体が該電解液で膨潤され得る温度および圧力下に保持することの特徴とする方法によって、上記のようなハイブリッド電解質を用いる電気化学

素子を確実に且つ効率よく製造し得ことを見出した。

さらに又、上記高分子多孔質成形体を電極と積層して積層体を得、該積層体に、上記の電解液によって該高分子多孔質成形体を実質的に膨潤され得ない温度および圧力下で、該電解液を含浸させて含浸積層体を得、該含浸積層体を該高分子多孔質成形体が該電解液で膨潤される温度および圧力下に保持することを特徴とする方法により、上記のようなハイブリッド電解質を用いる電気化学素子を確実に且つ効率よく製造することができることを見出した。

本発明は、上記の諸知見に基いて完成されたものである。

従って、本発明の一つの目的は、高いイオン伝導度を有し、高温安定性に優れ、且つ電極との接着性に優れたハイブリッド電解質を提供することにある。

本発明の他の一つの目的は、上記の特徴を有するハイブリッド電解質を確実に且つ効率よく製造する方法を提供することにある。

本発明のさらに他の一つの目的は、上記の特徴を有するハイブリッド電解質を用いた電池などの電気化学素子を確実に且つ効率よく製造する方法を提供することにある。

本発明の上記及び他の諸目的、諸特徴並びに諸利益は、次の詳細な説明及び請求の範囲の記載から明らかになる。

発明の詳細な説明

本発明の基本的な態様によれば、架橋された高分子セグメントを含む高分子母材及び該母材中に分散している複数の気泡からなる高分子多孔質成形体と、電解質の水系または非水系溶媒溶液および液状電解質からなる群より選ばれる電解液とを包含してなり、該高分子多孔質成形体が該電解液で含浸・膨潤されており、該高分子母材のゲル分率が20～75%である、ハイブリッド電解質が提供される。

次に、本発明の理解を容易にするために、まず本発明の基本的特徴および諸態様を列挙する。

1. 架橋された高分子セグメントを含む高分子母材及び該母材中に分散している複数の気泡からなる高分子多孔質成形体と、電解質の水系または非水系溶媒溶液および液状電解質からなる群より選ばれる電解液とを包含してなり、該高分子多孔質成形体が該電解液で含浸・膨潤されており、該高分子母材のゲル分率が20～75%である、ハイブリッド電解質。

2. 該高分子母材のゲル分率が30～70%である、前項1に記載のハイブリッド電解質。

3. 該高分子母材のゲル分率が35～65%である、前項1に記載のハイブリッド電解質。

4. 該複数の気泡が該高分子多孔質成形体を貫通する孔を有する連続気泡である、前項1～3のいずれかに記載のハイブリッド電解質。

5. 該高分子多孔質成形体の空隙率が30～95%の範囲にある、前項1～4のいずれかに記載のハイブリッド電解質。

6. 膜厚1～500 μm のシート状であることを特徴とする前項1～5のいずれかに記載のハイブリッド電解質。

7. 該高分子母材が、フッ化ビニリデンポリマーまたはアクリロニトリルポリマーからなることを特徴とする、前項1～6のいずれかに記載のハイブリッド電解質。

8. 該架橋された高分子セグメントの架橋構造が、電子線照射または γ 線照射によって形成されていることを特徴とする、前項1～7のいずれかに記載のハイブリッド電解質。

9. 架橋された高分子セグメントを含む高分子母材及び該母材中に分散している複数の気泡からなる高分子多孔質成形体に、電解質の水系または非水系溶媒溶液および液状電解質からなる群より選ばれる電解液によって該高分子多孔質成形体

が実質的に膨潤され得ない温度および圧力下で、該電解液を
含浸させて含浸高分子多孔質成形体を得、該含浸高分子多孔
質成形体を該高分子多孔質成形体が該電解液で膨潤され得る
温度および圧力下に保持することを特徴とする、ハイブリッ
ド電解質の製造方法。

1 0 . 該複数の気泡が該高分子多孔質成形体を貫通する孔を
有する連続気泡である、前項 9 に記載のハイブリッド電解質
の製造方法。

1 1 . 該高分子母材がフッ化ビニリデンポリマーまたはアク
リロニトリルポリマーからなることを特徴とする、前項 9 ま
たは 1 0 に記載のハイブリッド電解質の製造方法。

1 2 . 該電解液が電解質の非水系溶媒溶液および液状電解質
からなる群から選ばれる電解液である、前項 9 ～ 1 1 のいづ
れかに記載のハイブリッド電解質の製造方法。

1 3 . フッ化ビニリデンポリマーまたはアクリロニトリルポ
リマーからなり、架橋された高分子セグメントを含む高分子
母材及び該母材中に分散している複数の気泡よりなる高分子
多孔質成形体に、電解質の非水系溶媒溶液および液状電解質
からなる群から選ばれる電解液を常圧下 3 5 °C 以下の温度で

含浸させて含浸高分子多孔質成形体を得、該含浸高分子多孔質成形体を常圧下 80℃以上の温度で加熱することを特徴とする、ハイブリッド電解質の製造方法。

14. 該複数の気泡が該高分子多孔質成形体を貫通する孔を有する連続気泡である、前項13に記載のハイブリッド電解質の製造方法。

15. 加熱温度が90℃以上である前項13または14に記載のハイブリッド電解質の製造方法。

16. 前項9～15のいずれかに記載の製造方法により製造された、ハイブリッド電解質。

17. 架橋された高分子セグメントを含む高分子母材及び該母材中に分散している複数の気泡よりなる高分子多孔質成形体に、電解質の水系または非水系溶媒溶液および液状電解質からなる群より選ばれる電解液によって該高分子多孔質成形体を実質的に膨潤され得ない温度および圧力下で、該電解液を含浸させて含浸高分子多孔質成形体を得、該含浸高分子多孔質成形体を電極と積層して積層体を得、該積層体を該高分子多孔質成形体が該電解液で膨潤され得る温度および圧力下に保持することを特徴とする電気化学素子の製造方法。

18. 該高分子母材がフッ化ビニリデンポリマーまたはアクリロニトリルポリマーからなることを特徴とする、前項17に記載の電気化学素子の製造方法。

19. フッ化ビニリデンポリマーまたはアクリロニトリルポリマーからなり、架橋された高分子セグメントを含む高分子母材及び該母材中に分散している複数の気泡よりなる高分子多孔質成形体に、常圧下35℃以下の温度で電解質の非水系溶媒溶液液状電解質からなる群から選ばれる電解液を含浸させて含浸高分子多孔質成形体を得、該含浸高分子多孔質成形体を電極と積層して積層体を得、該積層体を常圧下80℃以上の温度で加熱することを特徴とする、電気化学素子の製造方法。

20. 加熱温度が90℃以上である、前項19に記載の電気化学素子の製造方法。

21. 架橋された高分子セグメントを含む高分子母材及び該母材中に分散している複数の気泡よりなる高分子多孔質成形体を電極と積層して積層体を得、該積層体に、電解質の水系または非水系溶媒溶液および液状電解質からなる群より選ばれる電解液によって該高分子多孔質成形体が実質的に膨潤さ

れ得ない温度および圧力下で該電解液を含浸させて含浸積層体を得、該含浸積層体を該高分子多孔質成形体が該電解液で膨潤され得る温度および圧力下に保持することを特徴とする電気化学素子の製造方法。

2 2 . 該高分子母材がフッ化ビニリデンポリマーまたはアクリロニトリルポリマーからなることを特徴とする、前項 2 1 に記載の電気化学素子の製造方法。

2 3 . フッ化ビニリデンポリマーまたはアクリロニトリルポリマーからなり、架橋された高分子セグメントを含む高分子母材及び該母材中に分散している複数の気泡よりなる高分子多孔質成形体を電極と積層して積層体を得、該積層体に、常圧下 3 5 °C 以下の温度で電解質の非水系溶媒溶液状電解質からなる群から選ばれる電解液を含浸させて含浸積層体を得、該含浸積層体を常圧下 8 0 °C 以上の温度で加熱することを特徴とする、電気化学素子の製造方法。

2 4 . 加熱温度が 9 0 °C 以上である、前項 2 3 に記載の電気化学素子の製造方法。

2 5 . 該電気化学素子が、電極として正極および負極を用いる電池であることを特徴とする、前項 1 7 ~ 2 4 に記載の電

気化学素子の製造方法。

26. 該電池が非水系電池であることを特徴とする、前項25に記載の電気化学素子の製造方法。

27. 該電池がリチウムイオン二次電池であることを特徴とする、前項26に記載の電気化学素子の製造方法。

28. 該電気化学素子の電極が集電体を設けた電極であり、且つその集電体がメッシュ集電体であることを特徴とする、前項17～27に記載の電気化学素子の製造方法。

29. 前項17～28のいずれかに記載の製造方法により製造された、電気化学素子。

本発明のハイブリッド電解質とは、液を含まないドライ系固体電解質と、従来からの液系電解質、すなわち、電解質化合物を水系又は非水系溶媒に溶解してなる電解液の中間的な性質を有する電解質で、高分子が溶液となって流れ出さない範囲で好ましくは高沸点の溶媒を多量に含んだ高分子固体電解質で、電解液を含みながらもゲル状の様相を示すことで、電解液の保持性を高めたものである。更に特定すれば、本発明のハイブリッド電解質は、架橋された高分子セグメントを

含み且つ20～75%のゲル分率を有する高分子母材及び該母材中に分散している複数の気泡からなる高分子多孔質成形体が、電解質の水系または非水系溶媒溶液および液状電解質よりなる群より選ばれる電解液で含浸・膨潤されてなるものである。

本発明でいう膨潤について説明する。一般に架橋されたポリマーが大過剰の溶媒や溶液で膨潤された場合大幅に体積が増加する。多くの場合、架橋されたポリマーは全ての方向に膨張するが、延伸などで応力がかかっていた場合には応力が緩和され、方向によっては縮小することもあるが、いずれにしても架橋されたポリマーが大過剰の溶媒や溶液で膨潤された場合には大きな変形が起こる。本発明において、或る圧力及び温度条件下において高分子多孔質成形体をその外形の体積の100倍以上の量の電解液中に浸漬した際に、浸漬前の高分子多孔質成形体と比較して長さ方向で10%を越える大きな変形を起こせば、該高分子多孔質成形体は該圧力及び温度条件下で膨潤し得るものであると定義する。

また、製造されたハイブリッド電解質が電解液で含浸・膨潤された状態であるかどうかは該ハイブリッド電解質から電解液を抽出して除去し、室温で乾燥したときの収縮率から確認することができる。即ち、該ハイブリッド電解質から、高分子母材を溶かさず電解液のみを溶解する溶媒に30分以上浸漬することにより電解液を抽出して除去し、室温で、必要

により真空中で固定せずに自由に乾燥したときの元のハイブリッド電解質に対する長さ方向の変化として求められる収縮率が10%を越えるものは、本発明においては含浸・膨潤されているものとする。本発明のハイブリッド電解質は、上記の定義に基づいた、電解液で含浸・膨潤された状態にある。

一般に、ハイブリッド電解質は、ポリマーを含む固体電解質を用いる、いわゆるポリマー電池用の電解質として用いられる場合には、シート状等の形状で用いられる。この場合、ハイブリッド電解質を機械的に電極と接触させておくことが困難なので、電極とは接着させておく必要がある。このとき、電極と電解質を接着させる方法としては、 $0.1 \sim 20 \text{ kg/cm}^2$ の圧力下、 $50 \sim 200^\circ\text{C}$ 程度に加熱することにより接着させるか、あるいはハイブリッド電解質の種類によっては室温で接着させる方法が一般的である。また、熱をかける場合には、ハイブリッド電解質を構成するポリマーを一部溶解させることで、接着剤的な役割を担わせることができる。このとき、ハイブリッド電解質と電極の接着性は、後記するように、ハイブリッド電解質の高分子多孔質成形体を構成する、架橋された高分子セグメントを含む高分子母材のゲル分率に左右される。

本発明のハイブリッド電解質の高分子母材のゲル分率は20～75%の範囲であることが必要である。ここで上限は好ましく70%であり、さらに好ましくは65%である。また

下限は好ましくは30%であり、さらに好ましくは35%である。ゲル分率が75%を越えると加熱により電極と接着する際に接着しにくくなり、電極との接着強度が低下する。またゲル分率が20%よりも低いと加熱時に変形し易くなり、高温安定性が乏しくなる。

前記したように、本発明のハイブリッド電解質は、高分子多孔質成形体が電解液で含浸・膨潤されてなり、該高分子多孔質成形体の高分子母材のみならず該高分子母材中に分散している気泡中にも電解液が含まれている。該高分子多孔質成形体をなす架橋された高分子セグメントを含む高分子母材は、ポリマーを架橋処理して得られる、架橋された高分子セグメントを含むポリマーからなる。このポリマーは架橋処理された後用いる電解液に膨潤可能なものであれば特に制限はないが、電気化学的に安定なものが好ましく、また高いイオン伝導性を有するポリマーが好ましい。このようなポリマーの具体例としては、ポリエチレンオキサイド、ポリプロピレンオキサイド、フッ化ビニリデンポリマー、アクリロニトリルポリマー、ポリ(メタ)アクリル酸オリゴエチレンオキサイド、ポリエチレンイミン、ポリアルキレンスルフィド、オリゴエチレンオキサイドを側鎖に有するポリホスファゼンやポリシロキサン、ナフィオン(米国、デュポン社製)やフレミオン(日本国、旭硝子株式会社製)等の分子内にイオン性基を有する高分子等を挙げることができる。フッ化ビニリデンポリ

マー及びアクリロニトリルポリマーは、単独重合体のみならず、共重合体を包含する。例えば、フッ化ビニリデンーヘキサフルオロプロピレン共重合体、フッ化ビニリデンートリフルオロエチレン共重合体、アクリロニトリルー（メタ）アクリル酸エステル共重合体、アクリロニトリルースチレン共重合体等もまた用いることができる。分子内にイオン性基を有する高分子を利用してリチウム電池に利用する場合にはイオン性基はリチウム塩であることが望ましい。これらのポリマー種の中で、高いイオン伝導度と強度を合わせ持つことからポリフッ化ビニリデン、フッ化ビニリデンーヘキサフルオロプロピレン共重合体等のフッ化ビニリデンポリマーや、ポリアクリロニトリル、アクリロニトリルー（メタ）アクリル酸エステル共重合体、アクリロニトリルースチレン共重合体等のアクリロニトリルポリマーが好ましい。フッ化ビニリデンポリマーがさらに好ましい。

これらのポリマーは、最終的には架橋処理により架橋された高分子セグメントを含むポリマーに変換して用いられる。ポリマーに架橋構造を導入することでハイブリッド電解質の高温安定性が高まる。ポリマーが架橋されていないと、ハイブリッド電解質を用いて作製した電池が高温にさらされたときに電池としての性能が不可逆的に変化したり、場合によってはポリマーの溶解による短絡が起こる。この架橋構造は重合時、高分子多孔質成形体の形成前、形成後のどの段階でも

導入することができる。多孔質形成体が電解液や可塑剤などを含んだ状態で架橋構造を導入してもよい。架橋の方法としては重合時に多官能のモノマーを添加する方法、重合後に電子線、 γ 線、X線、紫外線等の輻射エネルギーを照射する方法、やはり重合後にラジカル開始剤を含有させて熱や輻射エネルギー照射により反応させる方法等を用いることができる。重合後に架橋構造を導入する場合、新たに単官能または／および多官能のモノマー成分を共存させておくこともできる。これらの架橋方法の中でも、夾雑物や未反応官能基が残存しにくいので、重合後に電子線、 γ 線、X線、紫外線等の輻射エネルギーを照射する方法が好ましく、電子線や γ 線がさらに好ましい。

この架橋処理によりポリマーは架橋された高分子セグメントを含むポリマーとなる。このポリマーを高分子母材とする高分子多孔質成形体の場合、該高分子多孔質成形体を、架橋処理前のポリマーが電解液に溶解してしまう条件下で大過剰の該電解液中に浸漬しても、該高分子多孔質成形体が電解液で膨潤されるのみで、該高分子多孔質成形体全体が溶解することはない。このときの高分子母材の架橋の程度はゲル分率で表され、該高分子母材をその架橋処理前の母材ポリマーの良溶媒での抽出処理に付し、その抽出前後の重量変化から求めることができる。このとき、ハイブリッド電解質中の高分子母材のゲル分率は、電解液で膨潤させる条件によっては、

電解液で膨潤させる前の高分子多孔質成形体の高分子母材のゲル分率とは異なってくるので、直接ハイブリッド電解質のゲル分率を測定する必要がある。

ハイブリッド電解質中の高分子母材のゲル分率の測定方法を例示すれば以下になる。即ち、まずハイブリッド電解質を、架橋された高分子セグメントを含む高分子母材を溶かさず電解液のみを溶解する溶媒に30分以上浸漬することにより該ハイブリッド電解質から電解液を抽出して除去し、乾燥して得られる乾燥高分子母材の重量 (W_1) を求める。次に該乾燥高分子母材を150メッシュのステンレス製金網に包み、該ハイブリッド電解質の製造に用いた架橋処理前のポリマーの良溶媒から選ばれる溶媒中で所定時間加熱還流した後、抽出残留物を、同じく該ハイブリッド電解質の製造に用いた架橋処理前のポリマーの良溶媒から選ばれる溶媒で洗浄し、真空乾燥後、抽出残留物の重量 (W_2) を求める。このとき $(W_2/W_1) \times 100$ をゲル分率 (%) とする。上記乾燥高分子母材の加熱還流に用いる溶媒の量は重量比で該乾燥高分子母材の約100倍以上が用いられる。その溶媒の例としては、例えば架橋処理前のポリマーがフッ化ビニリデンポリマーの場合、N, N-ジメチルアセトアミドとアセトンの混合溶媒 (容積比7:3)、アクリロニトリルポリマーの場合はN, N-ジメチルアセトアミド単独が適当である。この場合、加熱還流の時間は2時間以上、真空乾燥の時間は7

0℃で4時間以上がよい。

本発明のハイブリッド電解質の高分子多孔質成形体は、高分子母材中に気泡が分散した構造を有する。このような構造を持つことにより、該高分子多孔質成形体を電解液で膨潤させて得られるハイブリッド電解質は、そのイオン伝導度が高く、且つ該高分子多孔質成形体に対する電解液の含浸性が高い。気泡の形状としては独立気泡でも該高分子多孔質成形体を貫通する孔を有する連続気泡でもかまわないが、特に上記した効果の後者を効率的に得るためには、該高分子多孔質成形体を貫通する孔を有する連続気泡であることが好ましい。

該高分子多孔質成形体の空隙率は30～95%の範囲にあることが好ましい。30%未満の空隙率では電解質を形成したときのイオン伝導度が十分に高くなく、好ましくは40%以上、さらに好ましくは50%以上、さらに好ましくは55%以上である。また95%を越えると膨潤後に十分な強度が得られにくく、好ましくは90%以下、さらに好ましくは85%以下、特に好ましくは80%以下である。

また、本発明のハイブリッド電解質に含まれる電解液の量もまた30～95重量%の範囲にあることが好ましい。液含量が30重量%未満ではイオン伝導度が十分に高くなく、好ましくは40重量%以上、さらに好ましくは50重量%以上、さらに好ましくは55重量%以上である。また液含量が95重量%を超えると十分な強度が得られにくく、好ましくは9

0重量%以下、さらに好ましくは85重量%以下、特に好ましくは80重量%以下である。

尚、高分子多孔質成形体の空隙率は、該高分子多孔質成形体の高分子母材の非溶媒を空隙内に充填し、該非溶媒の重量を測定することで求めることができる。例えば該高分子母材がフッ化ビニリデンポリマーまたはアクリロニトリルポリマーの場合、以下の方法で求めることができる。まず高分子多孔質成形体の乾燥重量（A）を測定しておき、次に該高分子多孔質成形体をエタノールに浸漬して親水化した後、水中に浸漬して含浸したエタノールを十分に水で置換し、表面の水分を拭き取った後の高分子多孔質成形体の重量（B）を測定する。重量AおよびBと高分子多孔質成形体の材質の真比重（d）から次の式により空隙率を計算する。

$$\text{空隙率 (\%)} = [(B - A) / (A / d + B - A)] \times 100$$

本発明のハイブリッド電解質の形状は使用する目的により異なるので一概には限定されないが、例えば、上記したいわゆるポリマー電池の電極間の電解質として用いる場合には、シート状、織布状、不織布状といった形状が好ましい。この場合のシート状ハイブリッド電解質の膜厚は、一般的には1～500 μ m程度のものが用いられ、好ましくは10～300 μ m、さらに好ましくは20～150 μ mがよい。上記のシート状ハイブリッド電解質の製造のために用いられる薄膜状高分子多孔質成形体の厚さの範囲も上記と同様であること

が好ましい。シート状ハイブリッド電解質又は薄膜状高分子多孔質成形体の膜厚が $1\mu\text{m}$ 未満では強度が不足し、電極と積層して電池とした際電極間で短絡しやすくなり、又一方、シート状ハイブリッド電解質又は薄膜状高分子多孔質成形体の膜厚が $500\mu\text{m}$ を越えると、ハイブリッド電解質として実効電気抵抗が高くなりすぎるうえ、例えばポリマー電池の電解質として用いた場合には体積当たりのエネルギー密度が低くなりすぎる。

本発明で用いる高分子多孔質成形体の製造方法は特に限定されないが、複数の気泡が該高分子多孔質成形体を貫通する孔を有する連続気泡である高分子多孔質成形体の製造方法としては、マイクロフィルターやウルトラフィルターを製造する方法を利用することができる。例えば日本国特開平3-215535号公報に記載の方法や日本国特公昭61-38207号公報に記載の方法、日本国特開昭54-16382号公報に記載の方法を利用することができる。簡単に述べれば、具体的には溶融法や湿式法が挙げられ、溶融法は重合体を可塑剤や無機粉体等と共に溶融後、平膜状に成形して平膜状成形体を得、該平膜状成形体に含まれる可塑剤や無機粉体等を抽出除去することにより目的とする高分子多孔質成形体を得るものである。また湿式法は重合体を界面活性剤や添加剤等と共に溶媒に溶解した溶液を得、該溶液をキャストして液膜を得、該液膜を該重合体の非溶媒中に浸漬することにより該

液膜を凝固させ、同時に溶媒や界面活性剤や添加剤等を洗浄除去することにより、目的とする高分子多孔質成形体を得るものである。

また、気泡が独立気泡からなる高分子多孔質成形体の製造方法としては、ポリマーを成形して得られる成形体に発泡剤を拡散させて発泡剤含有成形体を得、該発泡剤含有成形体を加熱する、あるいは減圧条件下に保持することによって独立気泡を形成させることにより、気泡が独立気泡からなる高分子多孔質成形体を得る方法等が利用できる。本発明の高分子多孔質成形体の製造方法としては、上記の方法を単独または併用して用いることができる。

次に、高分子多孔質成形体を電解液で膨潤させることにより本発明のハイブリッド電解質を製造する方法には特に制限はないが、少なくとも高分子多孔質成形体を含浸するだけの量の電解液が該成形体中に含浸存在する状態で、高分子多孔質成形体を、該高分子多孔質成形体が該電解液で膨潤され得る圧力および温度条件下に保持することで本発明のハイブリッド電解質を得ることができる。このとき、高分子多孔質成形体の外見上の変形を伴っても、伴わなくてもよい。高分子多孔質成形体の外見上の変形を伴わないというのは、電解液の含浸前の高分子多孔質成形体と、それから製造されたハイブリッド電解質とで外見上のサイズはほとんど変わっていないが、高分子多孔質成形体そのものは、前に定義した膨潤された状態にあることをいう。従って、本発明のハイブリッド

電解質は、膨潤の際高分子多孔質成形体の外見上の変形を伴わなくても、該ハイブリッド電解質から電解液を除去し室温で乾燥したときの長さ方向の変化として表わされる収縮率は10%を超える。

また、上記したように、本発明のハイブリッド電解質の高分子母材のゲル分率は限定されている。該高分子多孔質成形体を膨潤させる際、膨潤操作に用いる方法によっては該高分子母材の一部が電解液中に溶出するため、高分子母材のゲル分率が本発明の範囲から外れることがある。しかし、高分子多孔質成形体が自由には膨潤し得ない量（即ち、該成形体の膨潤が平衡膨潤度にまで達しないような量）の電解液で該高分子多孔質成形体を膨潤させる方法、あるいは該高分子多孔質成形体を膨潤させる温度と時間をコントロールする方法などにより、含浸時の該高分子母材の一部の溶出を抑え、該高分子母材のゲル分率が本発明の範囲に含まれるよう制御することも可能で、このような方法で本発明のハイブリッド電解質を製造することができる。

しかしながら、本発明に含まれる以下の方法により、本発明のハイブリッド電解質を効果的に製造することができる。即ち、まず高分子多孔質成形体に、電解液によって該高分子多孔質成形体を実質的に膨潤され得ない温度および圧力下で、電解液を含浸させ、含浸高分子多孔質成形体を得る。含浸させる方法としては、該高分子多孔質成形体を電解液浴中の電解液に浸す方法が一般的であるが、その他に該高分子多孔質

成形体に該電解液をスプレーする、あるいは塗布する等の方法を採用することができる。この段階では高分子多孔質成形体は膨潤していないので、該含浸高分子多孔質成形体は十分に強度が高く、また含浸によるサイズの変化もほとんどないので比較的自由に扱うことができる。次に上記の状態にある該含浸高分子多孔質成形体を電解液浴や電解液のスプレー装置、塗布装置等の含浸装置から取り出し、該含浸高分子多孔質成形体の周囲に余分な電解液が存在しないようにする。必要により滴を切る、表面を拭き取るなどしてさらに余分な電解液を除去する。また、該高分子多孔質成形体を電極と積層させて積層体を得、該積層体に、電解液によって該高分子多孔質成形体を実質的に膨潤され得ない温度および圧力下で、該電解液を含浸させて含浸積層体を得てもよく、その場合は、該含浸積層体に対して上記した操作と同様の操作を行えばよい。この状態での該含浸高分子多孔質成形体のイオン伝導度は必ずしも十分に高いものではないが、このままの状態あるいは電極と積層した状態で該含浸高分子多孔質成形体または該含浸積層体を該高分子多孔質成形体が該電解液で膨潤される温度及び圧力下に保持することにより、高分子多孔質成形体を電解液で膨潤させると、高いイオン伝導度を有する本発明のハイブリッド電解質を容易に得ることができる。特に、該含浸高分子多孔質成形体を電極との積層後に膨潤のための加熱を行うことにより、イオン伝導度の向上と電極との接着とを同時に達成することができる。

さらに本発明の方法を用いることにより、含浸時において電解液浴の電解液中に高分子母材の一部が溶出することがなく、電解液浴等の汚染を防ぐことができる。

先に示したように、一般に架橋ポリマーを溶媒や溶液中で自由に膨潤させると、膨潤度が平衡膨潤度に達するまで大きな変形を伴って膨潤する。また変形を抑制するために、膨潤に使われる液量をコントロールし、膨潤度が平衡膨潤度に達しないようにすることも著しく困難である。しかしながら、本発明の方法に従えば膨潤に使われる液量は空隙率により限定されることから膨潤率も限られ、膨潤による高分子多孔質成形体の大きな変形を避けることができ、強度低下も抑制される。したがって、本発明の方法は、強度の高い状態で高分子多孔質成形体を電極と積層できる上、膨潤による高分子多孔質成形体の変形が小さいという点で、電解液を含浸させる前か後の高分子多孔質成形体を、電解液で膨潤させる前に電極を積層した場合に特に有用である。尚、膨潤は通常は常圧で、高分子多孔質成形体の種類によっては必要により減圧下でまたは加圧下で行う。また、膨潤後には高分子多孔質成形体の気泡に由来するハイブリッド電解質の空泡内に電解液は残っていても残っていなくてもよいが、少なくともハイブリッド電解質の内部には液相を有していることが好ましく、該液相がハイブリッド電解質を貫通していることが好ましい。

即ち、本発明の好ましい1つの態様によれば、架橋された

高分子セグメントを含む高分子母材及び該母材中に分散している複数の気泡よりなる高分子多孔質成形体に、電解質の水系または非水系溶媒溶液および液状電解質からなる群より選ばれる電解液によって該高分子多孔質成形体を実質的に膨潤され得ない温度および圧力下で、該電解液を含浸させて含浸高分子多孔質成形体を得、該含浸高分子多孔質成形体を電極と積層して積層体を得、該積層体を該高分子多孔質成形体が該電解液で膨潤され得る温度および圧力下に保持することを特徴とする電気化学素子の製造方法が提供される。

又、本発明の他の好ましい態様によれば、架橋された高分子セグメントを含む高分子母材及び該母材中に分散している複数の気泡よりなる高分子多孔質成形体を電極と積層して積層体を得、該積層体に、電解質の水系または非水系溶媒溶液および液状電解質からなる群より選ばれる電解液によって該高分子多孔質成形体を実質的に膨潤され得ない温度および圧力下で該電解液を含浸させて含浸積層体を得、該含浸積層体を該高分子多孔質成形体が該電解液で膨潤され得る温度および圧力下に保持することを特徴とする電気化学素子の製造方法が提供される。

本発明において、高分子多孔質成形体が電解液に膨潤され得る温度および圧力とは、高分子多孔質成形体を所定の圧力下、所定の温度の電解液中に浸漬した際に、浸漬の前後での該高分子多孔質成形体の変形が長さ方向で10%を越える温

度および圧力をいう。従って、所定の温度及び圧力下で高分子多孔質成形体が電解液で膨潤されていることは、所定の温度及び圧力下で該高分子多孔質成形体を該電解液に浸漬したときの変形から確認することができる。しかし、上記製造方法、即ち、高分子多孔質成形体に、電解液によって該高分子多孔質成形体を実質的に膨潤され得ない温度および圧力下で、電解液を含浸させ、得られる含浸高分子多孔質成形体の周囲に余分な電解液が存在しないようにし、該含浸高分子多孔質成形体を、該高分子多孔質成形体が該電解液で膨潤されうる温度及び圧力下に保持することによって高分子多孔質成形体を電解液で膨潤させる方法では、膨潤前後で高分子多孔質成形体のサイズが変わらないので、上記の製造方法の途中で該高分子多孔質成形体が電解液で膨潤されたことをサイズの変化により直接確認することはできない。そのため、該高分子多孔質成形体が電解液で膨潤され得る温度及び圧力を別途確認しておく必要がある。

又、本発明において、該高分子多孔質成形体を実質的に該電解液で膨潤され得ない温度および圧力とは、本発明においては該高分子多孔質成形体を所定の圧力下所定の温度の電解液に含浸させたときに、該高分子多孔質成形体の変形が長さ方向で10%以内である温度及び圧力、または、高分子多孔質成形体を所定の圧力下、所定の温度の電解液に浸漬して得られる含浸高分子多孔質成形体から電解液を抽出して除去し

室温で乾燥したときの、抽出前の該含浸高分子多孔質成形体に対する該高分子多孔質成形体の長さ方向の収縮率が10%以内となるときの温度および圧力のことをいう。

本発明のハイブリッド電解質の製造方法で用いられるポリマーは、用いる電解液との組み合わせにより異なり、また逆に、用いる電解液の種類もまた用いるポリマーの種類により異なる。本発明のハイブリッド電解質に含まれる電解液は、電解質の水系または非水系溶媒溶液、および液状電解質よりなる群より選ばれ、一般には以下のようなものが用いられる。まず、水系または非水系溶媒溶液として用いられる電解質としては無機塩、有機塩、無機酸、有機酸のいずれも使用可能である。この例として、たとえばテトラフルオロホウ酸、ヘキサフルオロリン酸、過塩素酸、ヘキサフルオロ砒素酸、硝酸、硫酸、リン酸、フッ化水素酸、塩酸、臭化水素酸、ヨウ化水素酸などの無機酸、トリフルオロメタンスルホン酸、ヘプタフルオロプロピルスルホン酸、ビス（トリフルオロメタンスルホニル）イミド酸、酢酸、トリフルオロ酢酸、プロピオン酸などの有機酸、およびこれら無機酸、有機酸の塩が挙げられる。さらにこれらの無機酸、有機酸およびこれらの塩の混合物も使用可能である。この塩の電解質のカチオンとして、アルカリ金属、アルカリ土類金属、遷移金属、希土類金属、アンモニウムイオンなどを単独または混合状態で用いることができる。このカチオン種は使用する用途によって好ま

しい種が異なる。たとえば、本発明のハイブリッド電解質を用いてリチウム電池を構成する場合は、添加する電解質としてリチウム塩を用いることが好ましい。特に、リチウム2次電池の場合、広い電位領域を使用するため、電解質として電気化学的に安定なリチウム塩が好ましく、この例として、 $\text{CF}_3\text{SO}_3\text{Li}$ 、 $\text{C}_4\text{F}_9\text{SO}_3\text{Li}$ などのフルオロアルキルスルホン酸リチウム塩、 $(\text{CF}_3\text{SO}_2)_2\text{NLi}$ 等のスルホニルイミドリチウム塩、 LiBF_4 、 LiPF_6 、 LiClO_4 、 LiAsF_6 を挙げることができる。これらの電解質の溶液中における適正な濃度は使用する目的により異なるが、一般には0.1mol/リットル～飽和溶解度の範囲で用いられ、好ましくは0.5～5mol/リットル、さらに好ましくは0.5～2mol/リットルの範囲で用いられる。

次にこれらの電解質を溶解する溶媒としては、水、アルコール等、化学的に安定で電解質を溶解するものであればよいが、特にリチウム電池のように非水系電解液として使用する場合には、エチレンカーボネート、プロピレンカーボネート、ジメチルカーボネート、ジエチルカーボネート、メチルエチルカーボネート等のカーボネート化合物、テトラヒドロフラン、ジメトキシエタン、ジグリム、テトラグリム、オリゴエチレンオキシド等のエーテル化合物、 γ -ブチロラクトン、 β -プロピオラクトン等のラクトン化合物、アセトニトリル、プロピオニトリル等のニトリル化合物等を挙げるこ

ができる。

以上挙げた中で、用いるポリマーと電解液の組み合わせは、該ポリマーを用いて製造した高分子多孔質成形体が該電解液で膨潤される組み合わせであればよく、該高分子多孔質成形体が電解質を溶解する溶媒の沸点以下で電解液で膨潤される組み合わせが好ましく、該高分子多孔質成形体が電解質を溶解する溶媒の沸点以下で電解液で膨潤され得るが、室温では実質的に膨潤され得ない組み合わせが特に好ましい。このような組み合わせの一例としては、エチレンカーボネートやプロピレンカーボネート等のカーボネート系の溶剤を電解質の溶媒として用いた場合のポリマーとしては、ポリフッ化ビニリデンやフッ化ビニリデンを含む共重合体、ポリアクリロニトリル等の組み合わせを挙げることができる。このような組み合わせの場合、含浸温度は35℃以下が好ましく、膨潤のための加熱温度は80℃以上が好ましく、90℃以上がさらに好ましい。

本発明では最終的には高分子多孔質成形体を電解液で膨潤させる必要がある。実際にはある圧力下該高分子多孔質成形体が電解液で膨潤され得るかされ得ないかは温度により左右され、該高分子多孔質成形体はある温度以下では該電解液によって実質的に膨潤され得ないということになる。実用上、電解液によって該高分子多孔質成形体を実質的に膨潤され得ない温度および圧力は常圧下、室温付近であることが好まし

い。尚、付け加えるならば、該高分子多孔質成形体が該電解液で膨潤され得るかされ得ないかは、該高分子多孔質成形体と該電解液が接触している時間にも左右されるが、ここでは常圧下ある温度で該高分子多孔質成形体を電解液に1時間程度浸漬してもほとんど変形しなければ該高分子多孔質成形体は該電解液によって実質的に膨潤され得ないものとみなす。

逆に、該高分子多孔質成形体が該電解液で膨潤され得ることは、所定の温度で該電解液に浸漬したときの変形から確認することができる。従って、ある圧力下加熱により高分子多孔質積層体を電解液で膨潤させる場合、そのために必要な最低の温度はポリマーと電解液の組み合わせによって異なるが、外観的には高分子多孔質成形体の変形から確認することができる。この場合、該高分子多孔質積層体を電極と積層した後では変形の確認は困難なので、別途膨潤に必要な最低の温度を確認しておくことが好ましい。膨潤に必要な最低温度は室温より高い温度で、且つ電解液中の溶媒の沸点以下の温度であることが好ましく、室温より20度以上高い温度であることがさらに好ましい。また、該高分子多孔質積層体を電極と積層してから加熱する場合は電極材料の電極としての活性が低下し始める温度以下であることが好ましい。加熱する時間は温度や伝熱の状態にもよるので一概には決められないが、一般には2分間以上、好ましくは10分間以上、さらに好ましくは30分間以上加熱することが望ましい。なお、膨潤す

るために必要な最低温度よりも充分高い温度であれば2分間程度の加熱で充分である。

上記の本発明のハイブリッド電解質の製造方法を用いて電池等の電気化学素子を製造する方法としては、前記したように、まず高分子多孔質成形体に電解液を含浸させて含浸高分子多孔質成形体を得、該含浸高分子多孔質積層体を電極と積層して積層体を得、該積層体を加熱する方法、高分子多孔質成形体に電極を積層して積層体を得、該積層体に電解液を含浸させて含浸積層体を得、該含浸積層体を加熱する方法があり、そのどちらも採用することができる。後者の方法において集電体を有する電極を用いる場合は、集電体にメッシュ状のものをを用いることにより効率よく液を含浸させることができる。また積層体の形状としてはシート状やロール状、折りたたみ構造やシートの積層体とすることができる。

本発明の電気化学素子を製造する方法において、用いられる電極材料は製造される電気化学素子の種類により異なるが、例えば電気化学素子がリチウム電池の場合、正極および負極としてリチウムの吸蔵放出が可能な物質が用いられる。この正極物質として、負極に対し高い電位を有する材料を選ぶ。この例として、 $\text{Li}_{1-x}\text{CoO}_2$ 、 $\text{Li}_{1-x}\text{NiO}_2$ 、 $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ 、 $\text{Li}_{1-x}\text{MO}_2$ ($0 < x < 1$) (MはCo、Ni、Mn、Feの混合体)、 $\text{Li}_{2-y}\text{Mn}_2\text{O}_4$ ($0 < y < 2$)、 $\text{Li}_{1-x}\text{V}_2\text{O}_5$ 、 $\text{Li}_{2-y}\text{V}_2\text{O}_5$ ($0 < y < 2$)、 $\text{Li}_{1.2-x}$

Nb_2O_5 ($0 < x' < 1.2$) などの酸化物、 $Li_{1-x}TiS_2$ 、 $Li_{1-x}MoS_2$ 、 $Li_{3-z}NbSe_3$ ($0 < z < 3$)、などの金属カルコゲナイド、ポリピロール、ポリチオフェン、ポリアニリン、ポリアセン誘導体、ポリアセチレン、ポリチエニレンビニレン、ポリアリレンビニレン、ジチオール誘導体、ジスルフィド誘導体などの有機化合物を挙げることができる。

また負極として、上記正極に対して低い電位を有する材料を用いる。この例として、金属リチウム、アルミニウム・リチウム合金、マグネシウム・アルミニウム・リチウム合金などの金属リチウム、グラファイト、コークス、低温焼成高分子などの炭素系材料、 SnM 系酸化物 (M は Si 、 Ge 、 Pb を表す)、 $Si_{1-y}M'_yO_2$ (M' は W 、 Sn 、 Pb 、 B などを表す)の複合酸化物、酸化チタン、酸化鉄などの金属酸化物のリチウム固溶体、 Li_7MnN_4 、 Li_3FeN_2 、 $Li_{3-x}Co_xN$ 、 $Li_{3-x}NiN$ 、 $Li_{3-x}Cu_xN$ 、 Li_3BN_2 、 Li_3AlN_2 、 Li_3SiN_3 の窒化物などのセラミックス等が挙げられる。ただし、リチウムイオンを負極で還元して金属リチウムとして利用する場合は、導電性を有する材料であればよいので上記に限定されない。

このような正極及び負極は上記の材料を所定の形状に成形加工する。電極の形態として、連続体、または粉末材料をバインダーに分散したもののいずれも使用可能である。前者の

連続体の成形方法として、電解、蒸着、スパッタリング、CVD、熔融加工、焼結、圧縮などが用いられる。また、後者の方法は、粉末状の電極材料をバインダーとともに混合して成形する。このバインダー材料としてポリフッ化ビニリデン等のイオン伝導性高分子、スチレン・ブタジエン系ラテックス、テフロン系ラテックス等の非イオン伝導性高分子、金属などが用いられる。また、このバインダーに重合性モノマーや架橋剤を添加しておき、成形後に重合、架橋させることもできる。さらにバインダーの強度向上、変性等の目的で電子線、 γ 線、紫外線等の輻射エネルギーを照射することもできる。また、正極または負極材料の電子移動を行うために電極に電気抵抗の低い材料で集電体を設けることができ、集電体を基板として上記の方法で電極材料を成形したものを電極とすることができる。

電極を積層する場合には、電極に電解液をあらかじめ含浸させておいてもよい。このとき電極に含浸された電解液の存在下、電解液を含浸した高分子多孔質成形体またはハイブリッド電解質と電極との積層体を加熱することで両者の接着性は格段に高めることができる。

本発明のハイブリッド電解質を用い、および／または本発明の方法で製造される電気化学素子としては、リチウム電池をはじめとする1次電池や2次電池の他、光電気化学デバイスや電気化学センサー等種々の電気化学素子を挙げることが

できる。

以上のように、本発明のハイブリッド電解質は、高いイオン伝導度を有し、高温安定性に優れ、そのうえ電極との接着性に優れた特徴を有する。また、ハイブリッド電解質や電気化学素子製造に、本発明の製造方法を用いれば、製造中において含浸高分子多孔質成形体の強度も大きく、電解液での膨潤前後での高分子多孔質成形体の寸法変化も小さいことから、上記の特徴を有するハイブリッド電解質や高性能の電気化学素子を効率よく製造することができ、さらには製造中に高分子母材の一部が電解液中に溶出することがないので、電解液浴等の含浸装置を汚染することもないため、産業上、極めて有用である。本発明のハイブリッド電解質はいわゆるポリマー電池用の電解質としたときに特に有用なものである。

発明を実施するための最良の形態

以下に実施例および比較例によって本発明を具体的に説明するが、これらは本発明の範囲を限定するものではない。

次の諸特性の測定は、以下の方法で行った。

高分子多孔質成形体の空隙率：

まず高分子多孔質成形体の乾燥重量（A）を測定しておき、次にこの高分子多孔質成形体をエタノールに浸漬して親水化した後、水中に浸漬して含浸したエタノールを十分に水で置換し、表面の水分を拭き取った後の高分子成形体の重量（B）を測定した。重量AおよびBと高分子多孔質成形体の材質の真比重（d）から次の式により空隙率を計算した。

$$\text{空隙率 (\%)} = [(B - A) / (A / d + B - A)] \times 100$$

高分子高分子多孔質成形体の収縮率および母材のゲル分率：

まず作製したハイブリッド電解質の一部を切り出し、エタノールに30分以上浸漬することにより電解液を抽出して除き、室温で真空乾燥して得られる乾燥高分子母材の重量を求めた。このときの該乾燥高分子母材の元のハイブリッド電解質に対する長さ方向の変化から収縮率を求めた。次に該乾燥高分子母材を150メッシュのステンレス製金網に包み、該乾燥高分子母材の1000倍以上の量の溶媒（高分子母材がフッ化ビニリデンポリマーの場合はN，N-ジメチルアセトアミドとアセトンの混合溶媒（容積比7：3）、アクリロニトリルポリマーの場合はN，N-ジメチルアセトアミド単独）

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中で4時間加熱還流した後、アセトンに5分間浸漬して洗浄し、70℃で6時間真空乾燥後、抽出残留物の重量を求めた。このときの重量を、電解液を抽出した後の高分子母材の乾燥重量で割った値をゲル分率とした。

・イオン伝導度は、ハイブリッド電解質を金属電極で挟み込むことにより電気化学セルを構成し、該電気化学セルの電極間に交流電圧を印可し交流インピーダンス法により測定した複素数インピーダンスのコールコールプロットにおける実数インピーダンス切片、該ハイブリッド電解質の厚さ、ならびに該金属電極の面積から計算した。

実施例 1

＜ハイブリッド電解質の作製＞

フッ化ビニリデンーヘキサフルオロプロピレン共重合体（ヘキサフルオロプロピレン5重量%）17.3重量部、平均分子量200のポリエチレングリコール11.5重量部、ジメチルアセトアミド71.2重量部からなる溶液を作り、この溶液100gに対してポリオキシエチレンソルビタンモノオレエート（日本国、花王アトラス（株）製、商品名Tween 80）を0.8ml加え、均一な溶液とした。その後、該溶液を室温でガラス板上にキャストすることにより、膜厚200μmの液膜を作製した。該液膜を直ちに70℃の水中に浸漬して凝固させた後、水、アルコールで洗浄後乾燥し

て、膜厚 $52\ \mu\text{m}$ 、空隙率 76% の高分子多孔質薄膜を作製した。さらに該高分子多孔質薄膜に電子線照射（照射量 $15\ \text{Mrad}$ ）し、架橋された高分子多孔質薄膜を作製した。

エチレンカーボネート／プロピレンカーボネートの $1:1$ 混合溶媒に LiBF_4 を $1\ \text{mol/l}$ の濃度で溶かした溶液を電解液として用いた。上記架橋された高分子多孔質薄膜を室温で上記電解液中に浸漬したところ、直ちに電解液が含浸し、透明な含浸多孔質薄膜が容易に得られた。該含浸多孔質薄膜の表面に付着した、含浸されなかった過剰の電解液は拭き取って除去した。このとき含浸による架橋された高分子多孔質薄膜のサイズの変化は長さ方向で 5% であった。該含浸多孔質薄膜を2枚のガラス板で挟み、 100°C のオーブンで2時間保持し、ハイブリッド電解質シートを作製した。このとき、加熱による上記含浸多孔質薄膜のサイズの変化は認められなかった。該ハイブリッド電解質シートの一部を切り出し、電解液を抽出して除去し、乾燥したときの収縮率は 16% 、高分子母材のゲル分率は 62% であった。一方、上記架橋された高分子多孔質薄膜を上記の電解液に 100°C で1時間浸漬したところ、サイズが長さ方向で 36% 増加しており、上記の温度は上記架橋された高分子多孔質薄膜が上記電解液で膨潤され得る温度であることが確認できた。

上記ハイブリッド電解質シートを2枚のステンレスシートで挟み込み、該ステンレスシートを電極としてインピーダン

ス測定（日本国、セイコーE G & G 社、389型インピーダンスメーターを使用）を行い、その結果から、室温におけるイオン伝導度を求めたところ、 1.3 mS/cm であった。

<電池の作製>

平均粒径 $10 \mu\text{m}$ の LiCoO_2 粉末とカーボンブラックを、ポリフッ化ビニリデン（日本国、呉羽化学工業（株）社製、KF1100）のN-メチルピロリドン溶液（5重量%）に混合分散してスラリーを作製した。尚、該スラリー中の固形分ならびにポリフッ化ビニリデンの重量比は、 LiCoO_2 （85%）、カーボンブラック（8%）、ポリフッ化ビニリデン（7%）とした。該スラリーを集電体として用いるアルミ箔の一方の面上にドクターブレード法で塗布乾燥して膜厚 $110 \mu\text{m}$ の塗膜からなる電極層を形成させることにより、 LiCoO_2 電極シート（正極）を作製した。

次に平均粒径 $10 \mu\text{m}$ のニードルコークス粉末に、上記と同じポリフッ化ビニリデンのN-メチルピロリドン溶液（5重量%）を混合してスラリーを作製した〔ニードルコークスとポリフッ化ビニリデンの重量比：ニードルコークス（92%）、ポリフッ化ビニリデン（8%）〕。該スラリーを集電体として用いる金属銅シートの一方の面上にドクターブレード法で塗布し、乾燥して膜厚 $120 \mu\text{m}$ の塗膜からなる電極

層を形成させることにより、ニードルコークス電極シート（負極）を作製した。

上記の LiCoO_2 電極シート、およびニードルコークス電極シートをそれぞれ 4 cm 角に切断し、上記電解液を含浸した。上記架橋された高分子多孔質薄膜に室温で上記電解液を含浸して得られた含浸多孔質薄膜を 4.5 cm 角に切断して、上記 2 種の電極シートが該含浸多孔質薄膜を挟むように積層（このとき、含浸多孔質薄膜とそれぞれの電極シートの電極層を密着させる）してニードルコークス（負極）／含浸多孔質薄膜／ LiCoO_2 （正極）の構成を有する電池を形成した。該電池を 2 枚のガラス板に挟んでクリップで止め、100℃で 2 時間保持した後室温まで放冷し、ガラス板からはずし、該電池の正極、負極の集電体にステンレス端子を取り付け、その電池を該ステンレス端子の先が外に出るようにして PET／Al／PE ラミネートフィルム（PET：ポリエチレンテレフタレートフィルム、Al：アルミニウム箔、PE：ポリエチレンフィルム）に挟み、ラミネーターでラミネートしてシート電池を作製した。

該シート電池を、充放電機（日本国、北斗電工社製 101SM6）に接続し、電流密度 1 mA/cm² の電流密度で充放電を行った。充電は、定電流放電後、4.2 V の定電位で行った。充電後の電極間電位は 4.2 V であり充電が確認できた。また放電は定電流放電で行い、電位が 2.7 V まで

低下したときに停止した。該シート電池の初回充放電効率は80%以上、2回目以降の充放電効率は99%以上で繰り返し充放電が可能であり、2次電池として作動することが確認できた。

該シート電池の充放電を10回繰り返した後、PET/A1/PEラミネートフィルムを剥がし、取り出した電池から電極シートを剥がそうとしたが、集電体（金属シート）のみが剥がれ、電解質と電極とは剥がれず、十分接着されていることを示した。そこで、集電体を剥がした状態で電極層ごと電解質層をエタノールで洗浄し、電解液を抽出して除いた後、表面の大半の電極層を削って除去したシートを得た。該シートを乾燥したときの収縮率は12%であった。さらに、該シート上に残った電極層を全て削り落として得られたシートについて上記方法で求めたゲル分率は64%であった。

比較例 1

実施例1で作製した高分子多孔質薄膜を4cm角に切断し、電子線を照射することなく実施例1と同じ電解液を含浸して含浸多孔質薄膜を得、表面についた過剰の電解液を拭き取り、該含浸多孔質薄膜をガラス板で挟んで100℃に加熱したところ、円形に変形したシートが得られた。尚、該シートに対して上記方法で求めたゲル分率は0%であった。また、加熱前の該含浸多孔質薄膜を用いて実施例1と同様にシート電池

を作製したが、短絡していて充電できなかった。

実施例 2

液膜の膜厚を $100\text{ }\mu\text{m}$ とした以外実施例 1 と同じ方法で製膜して膜厚 $25\text{ }\mu\text{m}$ 、空隙率 73% の高分子多孔質薄膜を作製した。さらに該高分子多孔質薄膜に電子線照射（照射量 15 Mrad ）し、架橋された高分子多孔質薄膜を作製した。

上記の架橋された高分子多孔質薄膜を実施例 1 と同じ電解液に室温で浸漬したところ、直ちに容易に電解液が含浸し、透明な含浸多孔質薄膜が得られた。表面に付着した、含浸されなかった過剰の電解液は拭き取って除去した。このとき含浸による高分子多孔質薄膜のサイズの変化は認められなかった。該含浸多孔質薄膜を 2 枚のステンレスシートに挟み込むことにより電気化学セルを構成し、該ステンレスシートを電極としてインピーダンス測定を行い、その結果より求めた室温におけるイオン伝導度は 0.25 mS/cm であった。次に該電気化学セルを 100°C で 1 時間保持した後、室温まで放冷し、再度インピーダンス測定を行ったところ室温におけるイオン伝導度は 1.1 mS/cm であった。

同様に 15 mm 角に切断した上記含浸多孔質薄膜を 2 枚のガラス板で挟み込み、 100°C のオーブンで 1 時間保持したところ、長さ方向のサイズの変化は 1 mm 以下であった。加熱後の該薄膜はピンセットで容易に取り扱うことができた。

一方、該架橋された高分子多孔質薄膜を上記電解液中に100℃で10分間浸漬したところ、15mm角であったものが20mm角となっており、上記の温度は上記架橋された高分子多孔質成形体が上記電解液で膨潤され得る温度であることが確認できた。

比較例 2

実施例 2 において作製した架橋前の高分子多孔質薄膜を用い、実施例 2 と同様にして電解液を含浸した電気化学セルを作製し、100℃で1時間保持した後、室温まで放冷し、再度インピーダンス測定を行ったところ短絡していた。また、該高分子多孔質薄膜を同じ電解液に90℃で浸漬したところ、4分で溶解した。

実施例 3 および比較例 3

実施例 1 で作製した LiCoO_2 電極シート、ニードルコークス電極シートをそれぞれ2cm角に切断し、実施例 2 と同様の方法で得た含浸多孔質薄膜を2.3cm角に切断して、上記2種の電極シートが該シートを挟むように積層してニードルコークス（負極）／含浸多孔質薄膜／ LiCoO_2 （正極）の構成を持つ電池を作製した。ついで該電池の正極、負極の集電体にステンレス端子を取り付け、外部に導電可能な電極端子を有し、外気を遮断可能なガラス容器（以後、単に

「ガラスセル」と称する)の端子にそれぞれ接続してアルゴン雰囲気中で封入した。

該電池を2個作製し、一方は100℃で2時間保持した後室温まで放冷してから(実施例3)、もう一方はそのまま(比較例3)、以下のインピーダンス測定および充放電を行った。インピーダンス測定では比較例3の電池の内部抵抗は80Ωであったが実施例3の電池では30Ωであった。さらにそれぞれの電池について実施例1と同様に充放電を行ったところ、いずれの電池も初回充放電効率80%以上、2回目以降の充放電効率は99%以上で繰り返し充放電が可能であり、2次電池として作動することが確認できた。しかし、実施例3の電池では過電圧が50mVであったが比較例3の電池では100mVであり容量が低いものであった。

実施例4

実施例2で作製した架橋された高分子多孔質薄膜を、実施例1の2種の電極シートで挟み込み、積層体を作製した。該積層体を実施例1と同じ電解液に室温で1時間浸漬し、電解液を含浸させることにより電池を作製した。該電池表面の過剰の電解液は拭き取って除去した。ついで該電池の正極、負極の集電体にステンレス端子を取り付け、ガラスセルの端子にそれぞれ接続してアルゴン雰囲気中で封入した。該電池を100℃で2時間保持した後室温まで放冷してから実施例3

と同様にインピーダンス測定および充放電を行ったところ、インピーダンス測定では電池の内部抵抗は $30\ \Omega$ であった。定電流放電後、 $4.2\ \text{V}$ の定電位充電後の電極間電位は $4.2\ \text{V}$ であり充電が確認できた。また放電は定電流放電で行い、電位が $2.7\ \text{V}$ まで低下したときに止めた。該電池の初回充放電効率 80% 以上、2回目以降の充放電効率は 99% 以上で繰り返し充放電が可能であり、2次電池として作動することが確認できた。このときの過電圧は $30\ \text{mV}$ であった。

実施例 5

フッ化ビニリデン-ヘキサフルオロプロピレン共重合体の代わりにポリフッ化ビニリデンホモポリマー（米国、エルフアトケムノースアメリカ社製 Kynar 460）を用いた以外、実施例 1 と同様の方法で架橋された高分子多孔質薄膜を作製した。膜厚は $45\ \mu\text{m}$ 、空隙率は 71% であった。該架橋された高分子多孔質薄膜を実施例 1 と同様に電解液に浸漬したところ電解液が含浸し、透明な含浸多孔質薄膜が得られた。含浸時の該架橋された高分子多孔質薄膜のサイズの変化は長さ方向で 3% であった。該シートを2枚のガラス板で挟み、 $120\ ^\circ\text{C}$ のオーブンで2時間保持し、ハイブリッド電解質シートを作製した。このとき、加熱による含浸多孔質薄膜のサイズの変化は認められなかった。該電解質シートの一部を切り出し、電解液を抽出し、乾燥したときの収縮率は2

4%、高分子母材のゲル分率は69%であった。一方、該架橋された高分子多孔質薄膜を同じ電解液に120℃で1時間浸漬したところ、該薄膜のサイズは長さ方向で40%増加しており、上記の温度は該架橋された高分子多孔質薄膜が該電解液で膨潤され得る温度であることが確認できた。得られたハイブリッド電解質シートの室温におけるイオン伝導度は1.1 mS / cmであった。

実施例1で作製したLiCoO₂電極シート、ニードルコークス電極シートをそれぞれ4 cm角に切断し、実施例1と同じ電解液を含浸させた。上記電解質シートを4.5 cm角に切断して、上記の2種の電極シートが該電解質シートを挟むように積層してニードルコークス（負極）／電解質シート／LiCoO₂（正極）の構成を有する電池を作製した。該電池を120℃で1分間加熱プレスした後、該電池の正極、負極の集電体にステンレス端子を取り付け、端子の先が外に出るようにPET／Al／PEラミネートフィルムに挟み、ラミネーターでラミネートして、シート電池を作製した。

該シート電池を実施例1と同様に充放電を行ったところ、初回充放電効率80%以上、2回目以降の充放電効率は99%以上で繰り返し充放電が可能であり、2次電池として作動することが確認できた。

該シート電池の充放電を10回繰り返した後、PET／Al／PEラミネートフィルムを剥がし、取り出した電池から

電極シートを剥がそうとしたが、集電体（金属シート）のみが剥がれ、電解質と電極とは剥がれず、十分接着されていることを示した。

実施例 6

フッ化ビニリデンーヘキサフルオロプロピレン共重合体の代わりにポリフッ化ビニリデンホモポリマー（米国、エルフアトケムノースアメリカ社製 K y n a r 7 4 0）を用いた以外、実施例 1 と同様の方法で架橋された高分子多孔質薄膜を作製した。膜厚は $60\text{ }\mu\text{m}$ 、空隙率は 77% であった。該架橋された高分子多孔質薄膜を実施例 1 と同様に電解液に浸漬したところ電解液が含浸した透明な含浸多孔質薄膜が得られた。含浸時の該架橋された高分子多孔質薄膜のサイズの変化は長さ方向で 3% であった。該含浸多孔質薄膜を 2 枚のガラス板で挟み、 120°C のオーブンで 2 時間保持し、ハイブリッド電解質シートを作製した。このとき、加熱による上記含浸多孔質薄膜のサイズの変化は認められなかった。該電解質シートの一部を切り出し、電解液を抽出し、乾燥したときの収縮率は 24%、高分子母材のゲル分率は 40% であった。一方、該架橋された高分子多孔質薄膜を同じ電解液に 120°C で 1 時間浸漬したところ、長さ方向で 38% 増加しており、上記の温度は該架橋された高分子多孔質薄膜が該電解液で膨潤され得る温度であることが確認できた。該ハイブリッド電

解質シートの室温におけるイオン伝導度は 1.4 mS/cm であった。

該電解質を用い、実施例5と同様にシート電池を作製して充放電を行ったところ、初回充放電効率80%以上、2回目以降の充放電効率は99%以上で繰り返し充放電が可能であり、2次電池として作動することが確認できた。該シート電池の充放電を10回繰り返した後、PET/Al/PEラミネートフィルムを剥がし、取り出した電池から電極シートを剥がそうとしたが、集電体（金属シート）のみが剥がれ、電解質と電極とは剥がれず、十分接着されていることを示した。

比較例 4

実施例5で膨潤条件の確認に用いた架橋された高分子多孔質薄膜を用い、実施例5と同じ電解液に120℃で1時間浸漬して作製したハイブリッド電解質シートについて、その一部を切り出し、電解液を抽出し、乾燥したときの収縮率は36%、高分子母材のゲル分率を測定したところ、86%であった。この電解質の室温におけるイオン伝導度は 1.8 mS/cm であった。

該電解質シートを用い、実施例5と同様にシート電池を作製して充放電を10回繰り返したところ、各回の充放電効率は不安定で一定しなかった。充放電を10回繰り返した後、PET/Al/PEラミネートフィルムを剥がし、取り出し

た電池から電極シートを剥がしたところ、部分的にLiCoO₂やニードルコックス粒子が表面に残るものの、電解質から電極シートをほぼ剥がすことができたことから、電解質を電極シートの接着が不十分であることを示した。

実施例 7

市販のポリフッ化ビニリデン製多孔膜であるデュラポアGVHP（孔径0.22μm、膜厚125μm、空隙率75%、日本国、ミリポアジャパン社製）に電子線照射（照射量30Mrad）し、架橋された高分子多孔質薄膜を作製した。該架橋された高分子多孔質薄膜を実施例1と同様に電解液に浸漬したところ直ちに溶液が含浸し、透明な含浸多孔質薄膜が得られた。含浸時の該架橋された高分子多孔質薄膜のサイズは変化しなかった。該含浸多孔質薄膜を2枚のガラス板で挟み、120℃のオーブンで2時間保持し、ハイブリッド電解質シートを作製した。このとき、加熱による該含浸多孔質薄膜のサイズの変化は認められなかった。該ハイブリッド電解質シートの一部を切り出し、電解液を抽出し、乾燥したときの収縮率は20%、高分子母材のゲル分率は72%であった。一方、該架橋された高分子多孔質薄膜を同じ電解液に120℃で1時間浸漬したところ、長さ方向で40%増加しており、上記の温度は該架橋された高分子多孔質薄膜が該電解液で膨潤されうる温度であることが確認できた。得られたハイブリ

ッド電解質シートの室温におけるイオン伝導度は $1.2 \text{ mS} / \text{cm}$ であった。

該電解質シートを用い、実施例 5 と同様にシート電池を作製して充放電を行ったところ、初回充放電効率 80% 以上、2 回目以降の充放電効率は 99% 以上で繰り返し充放電が可能であり、2 次電池として作動することが確認できた。

該シート電池の充放電を 10 回繰り返した後、PET/A1/PE ラミネートフィルムを剥がし、取り出した電池から電極シートを剥がそうとしたが、集電体（金属シート）のみが剥がれ、電解質と電極とは剥がれず、十分接着されていることを示した。

比較例 5

フッ化ビニリデン-ヘキサフルオロプロピレン共重合体（米国、エルフアトケムノースアメリカ社製 Kynarf 1ex 2801）2 重量部、ジブチルフタレート 2 重量部、アセトン 10 重量部を 50℃ で溶解し、0.5 mm 厚にキャストしたものを風乾して膜厚 90 μm の薄膜を作製した。該薄膜からジブチルフタレートをエーテルで抽出して除き、乾燥して無孔質の薄膜を作製した。該無孔質薄膜に電子線照射（照射量 15 Mrad）し、架橋された無孔質薄膜とした。該架橋された無孔質薄膜を実施例 1 と同じ電解液に 50℃ で浸漬したところ、電解液で膨潤されたハイブリッド電解質シ

ートが得られた。このとき、膨潤によるサイズの変化は長さ方向で25%の増加であった。該電解質シートの一部を切り出し、電解液を抽出し、乾燥したときの収縮率は25%、高分子母材のゲル分率は55%であった。また該電解質シートの室温におけるイオン伝導度は0.3 mS/cmであった。

該電解質シートを用い、プレス温度を100℃とした以外、実施例5と同様にシート電池を作製して充放電を10回繰り返したところ、各回の充放電効率が低く、10回目の放電容量は初回の40%まで低下していて2次電池としては極めて不十分なものであった。

実施例8

実施例1で作製した架橋された高分子多孔質薄膜を100℃に予熱したシャーレ上に置き、やはり100℃に加熱した実施例1と同じ電解液を該薄膜の白色部分がなくなり全体が透明になるまで該薄膜全体にまんべんなく少量ずつ滴下した後、室温まで放冷することによりハイブリッド電解質シートを作製した。該ハイブリッド電解質シートのサイズは該架橋された高分子多孔質薄膜に比べ長さ方向で30%増加しており、膨潤していることが確認できた。該ハイブリッド電解質シートの一部を切り出し、電解液を抽出し、乾燥したときの収縮率は36%、高分子母材のゲル分率は70%であった。また該電解質シートの室温におけるイオン伝導度は1.6 m

S / c mであった。

該電解質シートを用い、プレス温度を100℃とした以外、実施例5と同様にシート電池を作製して充放電を行ったところ、初回充放電効率80%以上、2回目以降の充放電効率は99%以上で繰り返し充放電が可能であり、2次電池として作動することが確認できた。該シート電池の充放電を10回繰り返した後、PET / Al / PEラミネートフィルムを剥がし、取り出した電池から電極シートを剥がそうとしたが、集電体（金属シート）のみが剥がれ、電解質と電極とは剥がれず、十分接着されていることを示した。

実施例9

実施例1で作製したLiCoO₂電極シート、ニードルコークス電極シートをそれぞれ4cm角に切断し、やはり実施例1で作製した架橋された高分子多孔質薄膜を4.5cm角に切断して、上記の2種の電極シートが該架橋された高分子多孔質薄膜を挟むように積層してニードルコークス（負極）／高分子多孔質薄膜／LiCoO₂（正極）の構成を有する積層体を作製した。該積層体を2枚のガラス板に挟んでクリップで止め、100℃に予熱して立てておき、やはり100℃に加熱した実施例1と同じ電解液をガラス板の間に少量ずつ滴下した後、室温まで放冷することにより電池を作製した。滴下は余分な液が下に流れ出したところで止めた。その後、

ガラス板からはずし、該電池の正極、負極の集電体にステンレス端子を取り付け、端子の先が外に出るようにPET/A1/P Eラミネートフィルムに挟み、ラミネーターでラミネートしたシート電池を作製した。

該シート電池を用い、実施例1と同様に充放電を行ったところ、初回充放電効率80%以上、2回目以降の充放電効率は99%以上で繰り返し充放電が可能であり、2次電池として作動することが確認できた。該シート電池の充放電を10回繰り返した後、PET/A1/P Eラミネートフィルムを剥がし、取り出した電池から電極シートを剥がそうとしたが、集電体（金属シート）のみが剥がれ、電解質と電極とは剥がれず、十分接着されていることを示した。そこで、集電体を剥がした状態で電極ごとエタノールで洗浄し、電解液を抽出して除いた後、表面の大半の電極層を削って除去したシートを得た。該シートを乾燥したときの収縮率は14%であった。さらに、該シート上に残った電極層を全て削り落として得られたシートについて上記方法で求めたゲル分率は65%であった。

実施例10～11

ポリアクリロニトリル17重量部、ジメチルスルホキシド83重量部からなる溶液を作製し、該溶液を室温（実施例10）または60℃（実施例11）でガラス板上にキャストし、

膜厚 $100\ \mu\text{m}$ の液膜を得た後、該液膜を直ちに室温（実施例 10）または 70°C （実施例 11）の水中に浸漬して凝固させた後、水、アルコールで洗浄後、乾燥して膜厚がそれぞれ $95\ \mu\text{m}$ 、 $76\ \mu\text{m}$ 、空隙率がそれぞれ 78% 、 81% の高分子多孔質薄膜を作製した。次いでそれぞれの該高分子多孔質薄膜に電子線を $30\ \text{Mrad}$ 照射し、架橋された高分子多孔質薄膜を作製した。該架橋された高分子多孔質薄膜が架橋されていることはエチレンカーボネート／プロピレンカーボネート 1 : 1 混合溶媒に不溶であったことから確認した。

次に、それぞれの上記架橋された高分子多孔質薄膜を、 LiBF_4 をエチレンカーボネート／プロピレンカーボネート 1 : 1 混合溶媒に濃度が $1\ \text{mol/l}$ となるよう溶解して得られる電解液に室温で 30 分間浸漬し、該電解液が含浸した透明な含浸多孔質薄膜を得た。膜厚はそれぞれ $103\ \mu\text{m}$ 、 $85\ \mu\text{m}$ であり、またいずれの場合も含浸前後で架橋された高分子多孔質薄膜のサイズは変化しなかった。該含浸多孔質薄膜表面の過剰の電解液は拭き取って除去した。該含浸多孔質薄膜を 2 枚のステンレスシートで挟み込んで電気化学セルを構成し、インピーダンス測定を行なったところ、室温におけるイオン伝導度はそれぞれ $0.3\ \text{mS/cm}$ 、 $0.4\ \text{mS/cm}$ であった。次にそれぞれの該電気化学セルを 100°C で 1 時間保持した後、室温まで放冷し、再度インピーダンス測定を行ったところ室温におけるイオン伝導度はそれ

ぞれ 1.2 mS / cm (実施例 10)、1.4 mS / cm (実施例 11) であった。このとき、加熱の前後で含浸多孔質薄膜のサイズ変化はいずれの場合も認められなかった。

尚、該架橋された高分子多孔質薄膜をそれぞれ同じ電解液に 100℃で 1 時間浸漬したところ、いずれの場合も該電解液に膨潤した透明シートが得られ、膨潤後の該透明シートの面積はそれぞれ膨潤前の架橋された高分子多孔質薄膜に比べ 350%、290%に増加していた。

実施例 12

フッ化ビニリデン-ヘキサフルオロプロピレン共重合体 (米国、エルファトケムノースアメリカ社製 Kynar F1lex 2801) 17 重量部、ポリビニルピロリドン (日本国、東京化成社製、K-30) 15 重量部、N-メチルピロリドン 68 重量部からなる溶液を調製し、該溶液を 50℃で、ガラス板上にキャストし膜厚 200 μm の液膜を得た。該液膜を直ちに N-メチルピロリドン/水の混合溶媒 (重量比 75 / 25) 中に室温で浸漬して凝固させた後、水、アルコールで洗浄後乾燥して膜厚 61 μm、空隙率 64% の高分子多孔質薄膜を作製した。さらに該高分子多孔質薄膜に電子線照射 (照射量 10 Mrad) し、架橋された高分子多孔質薄膜を作製した。

該架橋された高分子多孔質薄膜を実施例 1 と同じ電解液に

室温で浸漬したところ、直ちに溶液が含浸し、透明な含浸多孔質薄膜が得られた。該含浸多孔質薄膜を2枚のガラス板で挟み、100℃のオーブンで2時間保持し、ハイブリッド電解質シートを作製した。このとき、加熱による含浸多孔質薄膜のサイズの変化は認められなかった。該電解質シートの一部を切り出し、電解液を抽出し、乾燥したときの収縮率は42%、高分子母材のゲル分率は58%であった。該ハイブリッド電解質シートの室温におけるイオン伝導度は1.3 mS/cmであった。

該電解質シートを用い、プレス温度を100℃とした以外、実施例5と同様にシート電池を作製して充放電を行ったところ、初回充放電効率80%以上、2回目以降の充放電効率は99%以上で繰り返し充放電が可能であり、2次電池として作動することが確認できた。該シート電池の充放電を10回繰り返した後、PET/A1/PEラミネートフィルムを剥がし、取り出した電池から電極を剥がそうとしたが、集電体（金属シート）のみが剥がれ、電解質と電極とは剥がれず、十分接着されていることを示した。

実施例 13

実施例 10 で作製した架橋された高分子多孔質薄膜に実施例 10 と同様に電解液を含浸し、含浸多孔質薄膜を得た。該含浸多孔質薄膜を 2 枚のガラス板で挟み、100℃のオーブンで 1 時間保持し、ハイブリッド電解質シートを作製した。このとき、加熱による該含浸多孔質薄膜のサイズの変化は認められなかった。該ハイブリッド電解質シートの一部を切り出し、電解液を抽出し、乾燥したときの収縮率は 50%、高分子母材のゲル分率は 37% であった。該ハイブリッド電解質シートの室温におけるイオン伝導度は 1.4 mS/cm であった。

該ハイブリッド電解質シートを用い、実施例 5 と同様にシート電池を作製して充放電を行ったところ、初回充放電効率 80% 以上、2 回目以降の充放電効率は 99% 以上で繰り返し充放電が可能であり、2 次電池として作動することが確認できた。

該シート電池の充放電を 10 回繰り返した後、PET/A1/PE ラミネートフィルムを剥がし、取り出した電池から電極シートを剥がそうとしたが、集電体（金属シート）のみが剥がれ、電解質と電極とは剥がれず、十分接着されていることを示した。

産業上の利用可能性

本発明のハイブリッド電解質は、イオン伝導度が高く、高温安定性に優れ、また電極と接着させる際の接着性に優れているので、リチウム電池を初めとする一次電池および二次電池、光電気化学デバイス、電気化学センサーなどの電気化学素子用の電解質として有用である。また、本発明の製造方法を用いることにより、上記のような優れた特徴を有する本発明のハイブリッド電解質および該電解質を用いた電気化学素子を確実且つ効率よく製造することができる。

請 求 の 範 囲

1. 架橋された高分子セグメントを含む高分子母材及び該母材中に分散している複数の気泡からなる高分子多孔質成形体と、電解質の水系または非水系溶媒溶液および液状電解質からなる群より選ばれる電解液とを包含してなり、該高分子多孔質成形体が該電解液で含浸・膨潤されており、該高分子母材のゲル分率が20～75%である、ハイブリッド電解質。
2. 該高分子母材のゲル分率が30～70%である、請求項1に記載のハイブリッド電解質。
3. 該高分子母材のゲル分率が35～65%である、請求項1に記載のハイブリッド電解質。
4. 該複数の気泡が該高分子多孔質成形体を貫通する孔を有する連続気泡である、請求項1～3のいずれかに記載のハイブリッド電解質。
5. 該高分子多孔質成形体の空隙率が30～95%の範囲にある、請求項1～4のいずれかに記載のハイブリッド電解質。
6. 膜厚1～500 μm のシート状であることを特徴とする請求

項 1 ～ 5 のいずれかに記載のハイブリッド電解質。

7. 該高分子母材が、フッ化ビニリデンポリマーまたはアクリロニトリルポリマーからなることを特徴とする、請求項 1 ～ 6 のいずれかに記載のハイブリッド電解質。

8. 該架橋された高分子セグメントの架橋構造が、電子線照射または γ 線照射によって形成されていることを特徴とする、請求項 1 ～ 7 のいずれかに記載のハイブリッド電解質。

9. 架橋された高分子セグメントを含む高分子母材及び該母材中に分散している複数の気泡からなる高分子多孔質成形体に、電解質の水系または非水系溶媒溶液および液状電解質からなる群より選ばれる電解液によって該高分子多孔質成形体を実質的に膨潤され得ない温度および圧力で、該電解液を含浸させて含浸高分子多孔質成形体を得、該含浸高分子多孔質成形体を該高分子多孔質成形体が該電解液で膨潤され得る温度および圧力下に保持することを特徴とする、ハイブリッド電解質の製造方法。

10. 該複数の気泡が該高分子多孔質成形体を貫通する孔を有する連続気泡である、請求項 9 に記載のハイブリッド電解質の製造方法。

11. 該高分子母材がフッ化ビニリデンポリマーまたはアクリロニトリルポリマーからなることを特徴とする、請求項9または10に記載のハイブリッド電解質の製造方法。

12. 該電解液が電解質の非水系溶媒溶液および液状電解質からなる群から選ばれる電解液である、請求項9～11のいずれかに記載のハイブリッド電解質の製造方法。

13. フッ化ビニリデンポリマーまたはアクリロニトリルポリマーからなり、架橋された高分子セグメントを含む高分子母材及び該母材中に分散している複数の気泡よりなる高分子多孔質成形体に、電解質の非水系溶媒溶液および液状電解質からなる群から選ばれる電解液を常圧下35℃以下の温度で含浸させて含浸高分子多孔質成形体を得、該含浸高分子多孔質成形体を常圧下80℃以上の温度で加熱することを特徴とする、ハイブリッド電解質の製造方法。

14. 該複数の気泡が該高分子多孔質成形体を貫通する孔を有する連続気泡である、請求項13に記載のハイブリッド電解質の製造方法。

15. 加熱温度が90℃以上である請求項13または14に

記載のハイブリッド電解質の製造方法。

16. 請求項9～15のいずれかに記載の製造方法により製造された、ハイブリッド電解質。

17. 架橋された高分子セグメントを含む高分子母材及び該母材中に分散している複数の気泡よりなる高分子多孔質成形体に、電解質の水系または非水系溶媒溶液および液状電解質からなる群より選ばれる電解液によって該高分子多孔質成形体を実質的に膨潤され得ない温度および圧力下で、該電解液を含浸させて含浸高分子多孔質成形体を得、該含浸高分子多孔質成形体を電極と積層して積層体を得、該積層体を該高分子多孔質成形体が該電解液で膨潤され得る温度および圧力下に保持することを特徴とする電気化学素子の製造方法。

18. 該高分子母材がフッ化ビニリデンポリマーまたはアクリロニトリルポリマーからなることを特徴とする、請求項17に記載の電気化学素子の製造方法。

19. フッ化ビニリデンポリマーまたはアクリロニトリルポリマーからなり、架橋された高分子セグメントを含む高分子母材及び該母材中に分散している複数の気泡よりなる高分子多孔質成形体に、常圧下35℃以下の温度で電解質の非水系

溶媒溶液液状電解質からなる群から選ばれる電解液を含浸させて含浸高分子多孔質成形体を得、該含浸高分子多孔質成形体を電極と積層して積層体を得、該積層体を常圧下80℃以上の温度で加熱することを特徴とする、電気化学素子の製造方法。

20. 加熱温度が90℃以上である、請求項19に記載の電気化学素子の製造方法。

21. 架橋された高分子セグメントを含む高分子母材及び該母材中に分散している複数の気泡よりなる高分子多孔質成形体を電極と積層して積層体を得、該積層体に、電解質の水系または非水系溶媒溶液および液状電解質からなる群より選ばれる電解液によって該高分子多孔質成形体を実質的に膨潤され得ない温度および圧力下で該電解液を含浸させて含浸積層体を得、該含浸積層体を該高分子多孔質成形体が該電解液で膨潤され得る温度および圧力下に保持することを特徴とする電気化学素子の製造方法。

22. 該高分子母材がフッ化ビニリデンポリマーまたはアクリロニトリルポリマーからなることを特徴とする、請求項21に記載の電気化学素子の製造方法。

23. フッ化ビニリデンポリマーまたはアクリロニトリルポリマーからなり、架橋された高分子セグメントを含む高分子母材及び該母材中に分散している複数の気泡よりなる高分子多孔質成形体を電極と積層して積層体を得、該積層体に、常圧下35℃以下の温度で電解質の非水系溶媒溶液状電解質からなる群から選ばれる電解液を含浸させて含浸積層体を得、該含浸積層体を常圧下80℃以上の温度で加熱することを特徴とする、電気化学素子の製造方法。

24. 加熱温度が90℃以上である、請求項23に記載の電気化学素子の製造方法。

25. 該電気化学素子が、電極として正極および負極を用いる電池であることを特徴とする、請求項17～24に記載の電気化学素子の製造方法。

26. 該電池が非水系電池であることを特徴とする、請求項25に記載の電気化学素子の製造方法。

27. 該電池がリチウムイオン二次電池であることを特徴とする、請求項26に記載の電気化学素子の製造方法。

28. 該電気化学素子の電極が集電体を設けた電極であり、

且つその集電体がメッシュ集電体であることを特徴とする、
請求項 17 ～ 27 に記載の電気化学素子の製造方法。

29. 請求項 17 ～ 28 のいずれかに記載の製造方法により
製造された、電気化学素子。

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP97/02056

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl⁶ H01B1/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl⁶ H01B1/12, H01M10/40, H01M6/22, C08L27/16, C08L33/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926 - 1997
Kokai Jitsuyo Shinan Koho	1971 - 1997
Toroku Jitsuyo Shinan Koho	1995 - 1997

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 02-230662, A (Tonen Corp.), September 13, 1990 (13. 09. 90), Page 2, upper right column, line 19 to lower left column, line 6, lower right column, line 13; page 3, lower right column, lines 6 to 8 (Family: none)	1 - 29
A	JP, 03-276508, A (Fuji Photo Film Co., Ltd.), December 6, 1991 (06. 12. 91), Claim; page 7, lower left column, lines 1 to 5, lower right column, lines 2 to 4 (Family: none)	1 - 29
A	JP, 58-069019, A (Kureha Chemical Industry Co., Ltd.), April 25, 1983 (25. 04. 83), Page 3, upper right column, line 20 to lower left column, line 8 & US, 4560851, A & GB, 2108786, B2 & DE, 3240726, C2	1 - 29

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

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"E" earlier document but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

September 9, 1997 (09. 09. 97)

Date of mailing of the international search report

September 24, 1997 (24. 09. 97)

Name and mailing address of the ISA/

Japanese Patent Office

Facsimile No.

Authorized officer

Telephone No.

A. 発明の属する分野の分類 (国際特許分類 (IPC))
Int Cl⁸ H01B1/12

B. 調査を行った分野

調査を行った最小限資料 (国際特許分類 (IPC))

Int Cl⁸ H01B 1/12、
H01M10/40、H01M 6/22、
C08L27/16、C08L33/00

最小限資料以外の資料で調査を行った分野に含まれるもの

日本国実用新案公報 1926-1997年
日本国公開実用新案公報 1971-1997年
日本国登録実用新案公報 1995-1997年

国際調査で使用した電子データベース (データベースの名称、調査に使用した用語)

C. 関連すると認められる文献

引用文献の カテゴリー*	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する 請求の範囲の番号
A	J P, 02-230662, A (東燃株式会社)、13. 9月. 1990 (13. 09. 90)、第2頁右上欄第19行から同頁左下欄第6行、同頁右下欄第13行、及び第3頁右下欄第6乃至8行、(ファミリーなし)	1-29
A	J P, 03-276508, A (富士写真フィルム株式会社)、6. 12月. 1991 (06. 12. 91)、特許請求の範囲、第7頁左下欄第1乃至5行、及び同頁右下欄第2乃至4行、(ファミリーなし)	1-29
A	J P, 58-069019, A (呉羽化学工業株式会社)、25. 4月. 1983 (25. 04. 83)、第3頁右上欄第20行から同頁左下欄第8行、& US, 4560851, A & GB, 2108786, B2 & DE, 3240726, C2	1-29

☐ C欄の続きにも文献が列挙されている。

☐ パテントファミリーに関する別紙を参照。

* 引用文献のカテゴリー

「A」特に関連のある文献ではなく、一般的技術水準を示すもの

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「O」口頭による開示、使用、展示等に言及する文献

「P」国際出願日前で、かつ優先権の主張の基礎となる出願

の日の後に公表された文献

「T」国際出願日又は優先日後に公表された文献であって出願と矛盾するものではなく、発明の原理又は理論の理解のために引用するもの

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「&」同一パテントファミリー文献

国際調査を完了した日

09. 09. 97

国際調査報告の発送日

24.09.97

国際調査機関の名称及びあて先

日本国特許庁 (ISA/J P)

郵便番号100

東京都千代田区霞が関三丁目4番3号

特許庁審査官 (権限のある職員)

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